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THE ORIGIN OF THE DEPOSITS OF SULPHIDE ORES OF THE MISSISSIPPI VALLEY.[1]

WILLIAM H. EMMONS.

GENERAL STATEMENT.

BETWEEN the Appalachian Mountains on the east and the Rocky Mountain Front on the west there is a great area known as the Interior Lowlands element of North America. This area is made up chiefly of Paleozoic rocks that are almost flat-lying or that dip at low angles. Igneous rocks intruding the Paleozoic rocks are found at a few places within the area, but the igneous masses are small and in general widely spaced. Faults and low folds are numerous and some of them are traced scores of miles. Except in local areas, however, the rocks are not highly faulted. Within this area sulphide ores are found at many places. The region contains the world's greatest lead ore district, the world's greatest zinc-lead district, the world's greatest barite district, the world's greatest fluorspar district, and considerable deposits of manganese and gossan iron ores. Because igneous rocks and fissure veins are relatively rare within this area, nearly all who have investigated the deposits in detail have concluded that the ores have no genetic relation to igneous rocks. They are believed to have formed by rain water that soaked into the ground, gathered metals by dissolving them from the country rocks, and finally precipitated the metals along fissures and in favorable beds. Recently detailed mapping in many parts of this area, carried on by

[1] Presidential Address, delivered before the Society of Economic Geologists, New York Meeting, Dec. 29, 1928.

various surveys, has shown that there is a more definite relation of the deposits to the larger structures than was generally known. All of the most important mineral bearing areas are in areas of extensive faulting or else they lie on the strikes of faults or zones of deformation that are traced for scores or even hundreds of miles. The conclusion is inevitable that the deposits show a structural control which suggests ascending waters from deep sources. This conclusion is supported by the occurrence of many of the larger deposits in limestone below shales and of some of the largest deposits in low anticlines below shales. The deposits of the Ozark region are arranged in a great system of zones which shows a normal sequence, namely: (1) specularite and pyrite, (2) pyrite and chalcopyrite, (3) zinc, lead and barite, (4) probably manganese ore and possibly fluorite. This order is standard for deposits that are connected generically with igneous rocks and supports the hypothesis that the ores of the Ozark region are connected with igneous rocks—that the deposits are cryptobatholithic and evidences of an underlying batholith are the dikes that are found within the area. The deposits of the upper Mississippi valley in Wisconsin and Illinois also show zones. A copper-bearing belt is almost surrounded by a zone of lead and zinc ores without appreciable copper.

Previous Work and Acknowledgments.—The deposits of the Mississippi valley have been described by many investigators whose papers are cited on following pages. Nearly all who have mapped the deposits and the areas containing them agree that the ores have formed by meteoric waters although a few see a connection with igneous processes. There are three hypotheses, rather sharply set off, that are designed to account for the deposits.

1. It is held that the deposits have formed by the agency of ground water descending or moving laterally through the rocks, and depositing the ores at the places they now occupy. This hypothesis, in one form or another, is supported by the investigations of Whitney, Chamberlin, Keyes, Blake, Winslow, Buckley, Buehler, Grant, Cox and Miser. Bain supports this theory to

account for the Wisconsin zinc deposits, but not for the Joplin, Missouri, deposits.

2. A second hypothesis states that the ores are derived from rocks below those in which they are found; that the metals were leached by ground water from the deeper seated rocks that rose as an artesian circulation to deposit the ores at the places in which they are now found. This theory is supported by Bain, Van Hise, Siebenthal and Smith and Ball. Bastin has suggested that the precipitation has taken place through the agency of anaerobic bacteria.

3. A third hypothesis, that the ores were formed by thermal waters ascending from deep sources was advocated by Jenney, Nason, Pirsson, Tarr, and Spurr.

In the past few years many geologic maps have been issued covering parts of the areas in which the sulphide ores of the Mississippi valley are found. These include maps of Missouri by H. A. Buehler, C. E. Siebenthal, Stuart Weller and others; maps of Kentucky by W. R. Jillson and associates of the Kentucky Geological Survey; maps of Illinois by F. W. DeWolf, M. M. Leighton and associates; and maps of Oklahoma by H. D. Miser, C. N. Gould, C. W. Honess and others. There is now a much better setting for the study of the deposits of the Mississippi valley than heretofore.

The data that are presented herewith are obtained chiefly from the reports and maps cited. I have made several brief visits to certain of the various districts described and I made a longer study during the summer of 1927. For many courtesies during that visit I wish to thank Dr. H. A. Buehler and Mr. E. T. Campbell. I wish to thank also Mr. W. H. Comins, Manager of the National Lead Company mines at St. Francois, Mr. P. A. Haines, Superintendent, and Mr. Earl B. Patton, Assistant Superintendent of the St. Joseph lead mines at Flat River, for the use of maps and for other courtesies. Dr. H. A. Buehler and Mr. C. E. Siebenthal have kindly verified certain geological sections.

STRUCTURAL FEATURES OF THE INTERIOR LOWLANDS SEGMENT.

The Interior Lowlands segment lies west of the Appalachian Mountains and north of the Ouchita-Arbuckle-Wichita Mountains segment (Fig. 1). The Appalachian Mountains extend from Newfoundland to Alabama. They are characterized by strong folds and closely spaced granitic intrusions many of which were formed near the close of the Paleozoic era. The system

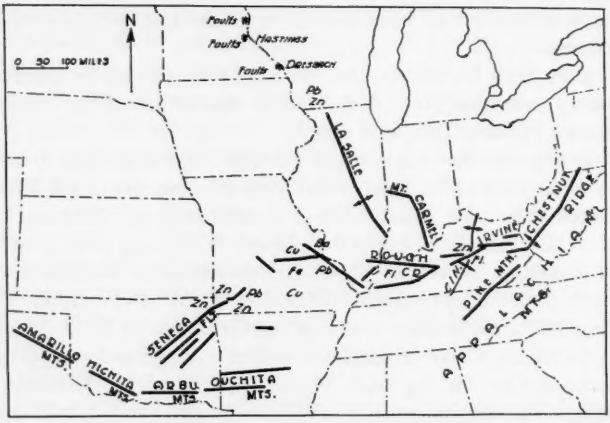

FIG. 1. Sketch showing relations of Appalachian and Ouchita Mountains and the major zone of deformation of the Mississippi valley. Heavy lines are faults except those marked with arrows to show anticlines and those designated mountain systems. The chief areas producing sulphide ores are noted.

of folds was deeply eroded before Cretaceous time and was covered at the southwest end by Cretaceous rocks. There is little evidence that the range bends to strike west at its south end but the Ouchita Mountains of Arkansas strike east and if continued would join the Appalachian Mountains. The Ouchita system also is characterized by strong folds similar to the folds of the Appalachian Mountains and by igneous intrusions. The folding took place near the close of Pennsylvanian time. The two moun-

tain systems are of about the same age and may be a single system although that is uncertain since the area between them is covered by the Mesozoic and later rocks of the Mississippi river embayment.

Westward the Ouchita Mountains belt of deformation extends through the Arbuckle and Wichita Mountain ranges to the Panhandle of Texas, where it is represented by the buried Amarillo Mountains. In this region a granite range lies below gently folded Permian rocks; the axis of the range is parallel to and in the strike of the Wichita Mountains of the Ouchita group. The Amarillo buried mountains extend almost to the foothills of the Rocky Mountains. Thus the area containing the sulphide ores of the Mississippi valley is almost surrounded by mountains. These mountains have influenced the structures of the great structural basin that lies between them.

The Pine Mountain fault lies at the southeast side of the basin. It is the outpost of the Appalachian mountain region and marks the limit of strong deformation on the northwest side of the mountains.

The most persistent zone of deformation in the Lowlands Element is the great belt of folding and faulting that extends southwest from Pennsylvania to Oklahoma known as the Warfield-Rough Creek Uplift. The zone includes the Chestnut Ridge anticline in Pennsylvania and West Virginia, the Warfield anticline in West Virginia, the Campton-Irvine fault in Kentucky, which lies east of the Cincinnati arch, the Rough Creek uplift in Kentucky west of the Cincinnati arch, and, in southeastern Illinois, the Hick's dome and Bald Hill uplift of Illinois, the Ozark Mountain uplift of Missouri and the Seneca fault zone of Oklahoma. (Fig. 2). This major zone of faulting and folding is more than 1,000 miles long. At certain places it is a fault or the axis of a fold. At other places it is a broad zone of deformation. At such places it is 50 miles wide or more.

Displacements along the faults of this great zone of deformation are at places known to be several hundred feet. In Perry County, Missouri, a great fault zone crosses the Mississippi

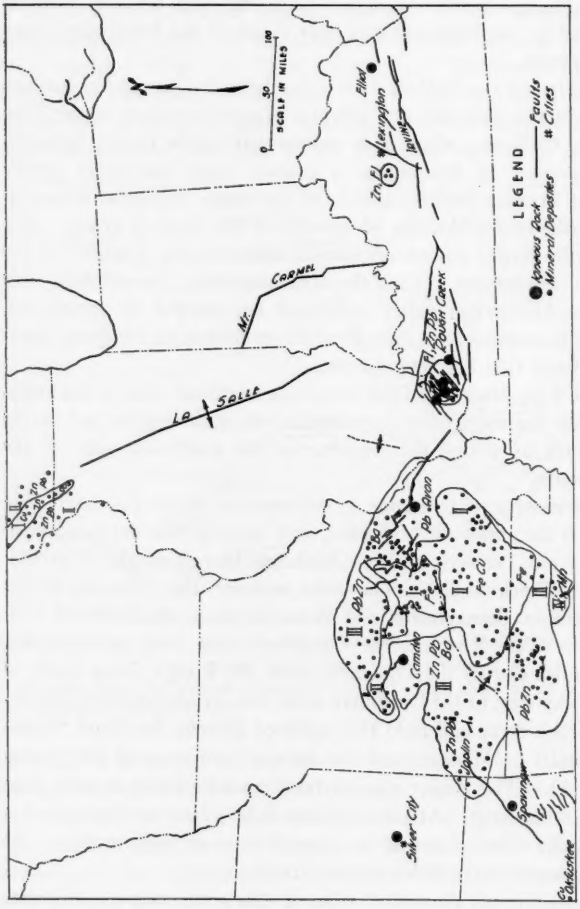

FIG. 2. Sketch showing major deformation, igneous rocks, and ore-bearing areas of Mississippi valley. Pre-Cambrian deposits omitted.

river near Wittenburg. This fault has been mapped by Weller, Flint, Ekblaw and others.[2] It extends southeast in Illinois about 30 miles; to the northwest in Missouri the fault zone is followed about 100 miles. It is a great group of faults rather than a single slip. On some of the faults the beds are overturned and there is a maximum vertical displacement of about 1,000 feet. In Missouri the faults of the zone are in part thrust faults. In Illinois the main fault is probably a tension fault. One of the faults of the Seneca group in Oklahoma has a displacement of more than 700 feet.

Along the major zone of deformation of the Mississippi valley lowlands area are found all of the igneous intrusives of the region and all but one of the chief mining districts producing sulphide ores (Fig. 2). The major zone of deformation is crossed by the Cincinnati anticline, and two zones of deformation extend north from it. These are the Mount Carmel fault of Indiana and the LaSalle fold of Illinois. In the strike of the latter near its north end are the gold occurrences near Eleroy, Illinois, and the lead-zinc deposits of southwestern Wisconsin and northwestern Illinois.

FIG. 2. Sketch showing major deformation, igneous rocks, and ore bearing areas of Mississippi valley. Pre-Cambrian deposits omitted.

VULCANISM IN THE MISSISSIPPI VALLEY.

The igneous rocks that crop out in the Mississippi valley lowlands are, as stated, near the axis of the uplift. They include the basic dikes of Elliot County in eastern Kentucky, the basic and acid dikes of Crittendon County in western Kentucky and of Hardin County in southern Illinois, the basic dikes near Avon in Ste. Genevieve County, Missouri, the pegmatites of Camden County, south central Missouri, and the granite of Spavinaw, northeastern Oklahoma. All of these rocks intrude Paleozoic sedimentary rocks and all may be of late Paleozoic age except the Spavinaw intrusive, which is probably older than the rocks that contain many of the sulphide ores of the Mississippi valley region.

In Woodson County, Kansas, at Silver City, sandstones of

[2] Weller, S., advance copy of geology of Ste. Genevieve County supplied through courtesy of Dr. H. A. Buehler, Mo. Geol. Survey; Flint, R. F., Thrust Faults in Southeastern Missouri, *Am. Jour. Sci.*, ser. 5, vol. 12, pp. 37–40, 1926.

Pennsylvanian age are cemented to form quartzites on the north side of an elongated structural dome. The sandstones contain quartz and pyrite and associated limestones contain hornblende and chlorite, suggesting contact metamorphism. On the Rose dome, 5 miles northeast of Silver City,[3] boulders of granite porphyry several feet in diameter are found at the top of a structural dome and quartz veins occur near by. These boulders probably represent the outcrop of a dike. A well drilled 3 miles southeast of the porphyry at a depth of 1,151 feet entered a basic igneous rock and passed it at 1,253 feet. Pennsylvanian strata lie above the basic rock and strata probably of Mississippian age are found below it. A well near by encountered a dacite dike.

The folding and faulting of the southern Appalachian region and the igneous intrusions to which probably all of the deposits of sulphide ores are generically related are probably of late Paleozoic age—the age of the Appalachian revolution. The folding and igneous intrusions of the Ouchita Mountains of central Arkansas, and southeastern Oklahoma are of the same age.

AGE OF THE SULPHIDE ORE DEPOSITS.

All of the deposits of sulphide ores in the Mississippi valley region may be of the same age. They are found in Carboniferous and older rocks and none of them are found in younger rocks. All of the igneous rocks noted may be of the age of the Appalachian revolution except the Spavinaw occurrence in northeastern Oklahoma and the basic intrusives near Murfreesboro, Pike County, Arkansas. The former is older than the sulphide deposits. The latter intrude Lower Cretaceous rocks and for that reason certain investigators have concluded that all of the igneous intrusives of the Mississippi valley region are probably of Cretaceous or later age and some of those who have seen a connection between the intrusives and the ore deposits are inclined to regard both as of Tertiary age, thus linking them with

[3] Twenhofel, W. H., "The Silver City Quadrangle," *Geol. Soc. Amer. Bull.*, vol. 28, pp. 419–430, 1917; Twenhofel, W. H., and Bremer, B., "An Extension of the Rose Dome Intrusive, Kansas," *Amer. Assoc. Pet. Geol.*, vol. 12, pp. 757–762, 1928.

ARKANSAS-MISSOURI BOUNDARY
OKLAHOMA
ARKANSAS
Intrusive Rock
Mineral Deposit
Fe Iron Bank
Fe Pevenston Springs
Fe Dewitt
Fe Saltzen
Fe Kellogg
Fe Hoadley
Fe Hurricane Diamonds
Fe Pike
Fe Johnson
Fe Berryville
Fe Carbonate House
Fe Wichita Belle
Fe Panther Co.
Fe Jackpot
Fe Bonanza
Fe Silver Hollow
Fe Hurricane Creek
Fe Wilhite's
Fe Gold Standard Lost Mine
Fe Willis
Fe Lead Hill
Fe Hopkins
Fe Gamble
Fe Rubenbark
Fe Mineral Fork
Fe Black Oak
Fe Mine
Fe Flint
Fe Cr
Fe Lucas
Fe Mammoth Spring
Fe Cherokee Prairie
Fe Pike
Fe Kellogg
Fe Little Rock
Fe Mc Kinney
Fe Mc Caskill Post
Fe Mc Caskill
Fe Mc Caskill Cave
Fe Hoadley
Fe Cadde Cap
Fe Silver City
Fe Northwestern Silver World Co
Fe Wattenburg
Fe Bullock
Fe Hochalgan
Fe Johnson
Fe Deerwen
Fe Pennsylvania Bluff
Fe Pike
Fe Cr
Fe Lucas
Fe Hurricane Diamonds

the great group of Tertiary ores of western America. This in my opinion is unwarranted. The basic rocks that intrude the Cretaceous at Murfreesboro are south of the Ouchita Mountains. The Ouchita Mountains, themselves, have a very definite metallogeny. The belt is intruded by many igneous masses in Arkansas and in southeastern Oklahoma. The ore deposits are small fissure veins with quartz, widely spaced and numerous. Probably all are in Paleozoic rocks. The Cretaceous and later rocks lie close to the metalliferous belt but they are barren of deposits of sulphide ores (Fig. 3). The intrusions of the Murfreesboro basic rocks seem not to have been attended by the deposition of metalliferous ores. The metallogeny of the Ouchita Mountains is similar in many respects to that of the southern Appalachian Mountains, although the mineralization is less vigorous. Fissure veins predominate and precious metals are commonly present in the ores.

The Ouchita Mountain belt of mineral deposits is not zoned with the Ozark belt but the two are separated by an area 75 to 100 miles wide in which sulphide ores and igneous rocks are wanting (Fig. 3). There is also a barren belt between the zone of the Mississippi valley uplift and the southern Appalachian belt of metallization. In this belt igneous rocks and ore deposits are wanting. The lead ores and barite deposits that constitute the northwest outposts of the zoned ores of the Appalachians do not overlap the outposts of the major belt of deformation of the Mississippi valley.

ZONAL ARRANGEMENTS OF THE ORES OF THE MISSISSIPPI VALLEY.

The principal ore deposits of the Mississippi valley show a rude zonal arrangement. All of the districts yielding sulphide ores in Missouri, Northeast Oklahoma, Kansas and northern Arkansas are included in a single zonal system. The fluorspar ores of southern Illinois and western Kentucky and the fluorite zinc and barite ores near Lexington, Kentucky, may be outliers of the same system, but that is uncertain. The zinc lead ores of southwestern Wisconsin and northwestern Illinois are not included in

this system, but occupy a separate center of metallization, which also shows zoning.

On the map showing zones (Fig. 4) there are omitted all pre-Cambrian iron ores and all ores of sedimentary origin. The tungsten-silver deposits at and near the Einstein mine in Madison County, eastern Missouri, are omitted also. They are in pre-Cambrian rocks and may be of pre-Cambrian age. If they are of late Paleozoic age they are erratic with respect to the zonal system. The central disc of the zonal system is not the most deeply eroded portion of the region. It lies west of the area of denuded pre-Cambrian rocks.

The mineral zones shown in the Ozark region are:

Zone I. Iron ore with specularite and pyrite; rose quartz crystals in gangue; lead and zinc practically wanting.

Zone II. Iron ore with pyrite; chalcopyrite copper ores, zinc and lead ore and barite appear in small amounts in certain deposits. Specularite and rose quartz are absent.

Zone III. Zinc ores, lead ores, barite, some iron ores with limonite and hematite; specularite and rose quartz absent; copper minerals rare.

Zone IV. Manganese ore with rhodochrosite; minute amounts of zinc, lead and copper.

Ozark Zone I.—Zone I is a rudely disc-like area mainly in Dent, Phelps, and Crawford counties, Missouri (Fig. 4). The rocks are chiefly of Cambro-Ordovician age, and are strongly faulted in the north and east part of the area. The mines are small but several of them have produced a few hundred thousand tons of ore.[4] Some of the deposits occupy sinks on an old erosion surface and many of them have been deeply weathered since they were formed. The specularite ore is associated with limonite that obviously has formed by the oxidation of iron sul-

[4] Crane, G. W., "The Iron Ores of Missouri," Mo. Bur. Geol. and Mines, vol. 10, pp. 1–434, 1911.

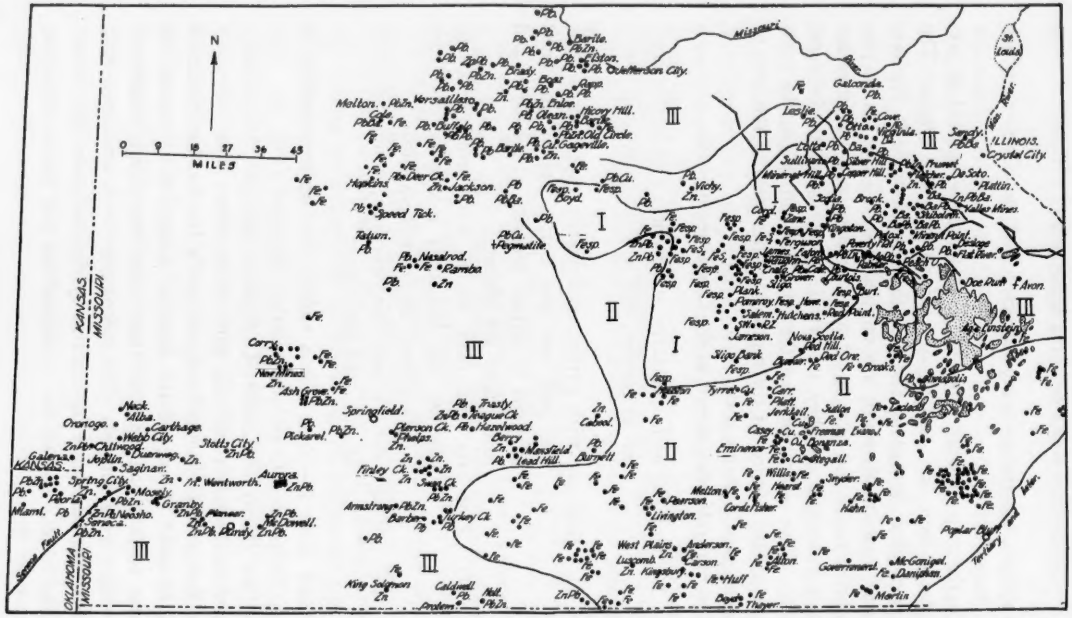

FIG. 4. Sketch of mineral zones of Ozark region, Missouri, Kansas, and Oklahoma. Zone I., specularite (Fesp.); zone II., pyrite, chalcopyrite; zone III., lead, zinc, barite. Stippled areas show pre-Cambrian rocks.

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[5] Crane, G.
10, pp. 54–64
[6] Bain, H.
Spurr, J. E.,

phide and in certain deposits the iron oxide ore is bottomed by ore containing iron sulphide. Pyrite and marcasite are commonly present and some of the marcasite at least is secondary. No pyrrhotite has been identified. Quartz is a common gangue mineral and stout crystals of quartz about an inch long showing the prism and pyramid are common. White quartz, amethystine quartz, rose quartz and smoky quartz are noted. Crane has noted these quartz crystals in several mines and I found them in all of the openings of specularite ore which I visited. Specularite has been noted in fifty mines or prospects of Zone I. No specularite is noted outside of them in Paleozoic rocks except some boulders with specularite in Franklin County on the northeast edge of the district. A few deposits with iron ore altered from pyrite and without specularite are found among the deposits of Zone I.

Ozark Zone II.—In Zone II the chief ores are iron ores that have formed by the oxidation of pyrite and marcasite. No specularite is noted in any of the deposits and rose quartz and amethystine quartz are probably absent. Pseudomorphs of pyrite are common.[5] The deposits are in general of small size but have been mined at scores of places. Zone II contains the copper ores near Sullivan in northeast Crawford County where a small copper smelter was operated, and the copper deposits of Shannon County,[6] one of which has produced $50,000 worth of copper ore. The copper ores have been mined at several other places in small amounts. About 200 deposits are found within Zone II. Lead and zinc ores and barite deposits are practically absent in Zone II although such ores are found at a few places. This zone extends into northern Arkansas where iron ores are found at Iron Bank, Diedrich and Salem mines (Fig. 3).

Ozark Zone III.—Zone III is the largest zone of the group and contains the most valuable deposits. These include: the deposits of the disseminated lead ores of the Flat River district

[5] Crane, G. W., "The Iron Ores of Missouri," Mo. Bur. Geol. and Mines, vol. 10, pp. 54–64, 1911.

[6] Bain, H. F., and Ulrich, E. O., U. S. Geol. Survey Bull. 267, pp. 1–52, 1905; Spurr, J. E., *Eng. and Min. Jour.* vol. 122, pp. 968–975, 1926.

FIG. 4. Sketch of mineral zones of Ozark region, Missouri, Kansas, and Oklahoma. Zone I., specularite (resp.); zone II., pyrite, chalcopyrite; zone III., lead, zinc, barite. Stippled areas show pre-Cambrian rocks.

and other disseminated lead ores in southeastern Missouri; the barite deposits of Washington and adjoining counties; the deposits of zinc and lead ores of Central Missouri; the zinc-lead deposits of the Joplin district and its extension into southeastern Kansas and northeastern Oklahoma; the lead and zinc ores of northern Arkansas and the eastward extension of this group in the area north of the Batesville manganese district, Arkansas. In Zone III about 300 mining districts, mines and occurrences of ore are mapped. All of them contain lead, zinc or barite and most of them contain two or all of these materials. Rose quartz is not known to be present; at only one place is specularite found in the ores, this being the doubtful occurrence of boulders in Franklin County already noted. Occurrences of pyritic iron ores without lead or zinc are rare and deposits of workable pyrite iron ores without lead or zinc are practically wanting. A little copper ore is found in the Cornwall district 8 miles southwest of Ste. Genevieve and copper with some nickel and cobalt occurs in mines at Lamotte and near Fredericksburg. These occurrences suggest a batholithic "high" passing southwest through Avon where basic dikes outcrop but the zone is not clearly defined and is not marked on the map (Fig. 4). The barite and lead district of Washington County lies directly east of Zone I. For about 20 miles along the border of Zone I the pyritic iron ores are wanting or undiscovered.

Flat River.—The disseminated lead district about 60 miles south of St. Louis is the premier mining district of the Mississippi valley and has produced about a billion dollars' worth of lead with small amounts of zinc, silver, nickel and cobalt. The rocks of this district are nearly flat-lying Paleozoic sedimentary rocks which lie unconformably on pre-Cambrian granites and porphyries.[7] No post-Cambrian intrusives are noted except some basic dikes near Avon. The section is given below.

[7] Buckley, E. R., "Geology of the Disseminated Lead Deposits of St. Francis and Washington Counties, Missouri, Mo. Bur. Geol. and Mines, vol. 9, pp. 1–259, 1909; Buehler, H. A., "Mineral Resources of Missouri," Mo. Bur. Geol. and Mines, pp. 1–34, 1918; Buehler, H. A., "Geology and Mineral Resources of the Ozark Region." *Am. Inst. Min. Eng. Trans.*, vol. 58, pp. 389–408, 1918; Spurr, J. E., *Eng. and Min. Jour.*, Dec. 18, 1926; Jan. 29, 1927; Nason, F. F., "The Disseminated Lead

Section of disseminated lead-bearing district, Missouri, after Buckley and Buehler.

Potosi		limestone and chert, contains barite and ores of lead and silver north of the main lead district.
Doe Run	47′	dolomite, argillaceous.
Derby	38′	dolomite.
Davis	169′	shale, cap rock of main lead-bearing formation.
Bonneterre	366′	dolomite with thin layers of dark shale, main lead-bearing formation.
LaMotte	0–300′	sandstone; valuable lead ore deposits at places.
Pre-Cambrian		
Granite and porphyry.		

The sedimentary rocks lie in relatively gentle folds. Large faults are found within the district and also to the east, north and west of the district. Some of these faults are traced many miles. A few of the faults are shown in Fig. 5. Although the rocks in the main are only gently folded, at places dips of 20° are noted and some of the folds may be traced for considerable distances. The lead ore lies below the Davis shale in the Bonneterre dolomite. The Davis shale which covers the dolomite appears to have been an effective barrier that halted the rising solutions that deposited the ores.

A very considerable number of the largest deposits of lead ore are found below gentle anticlines (Fig. 6) and near unconformities where the Paleozoic rocks lap against and dip away from the pre-Cambrian basement. The ore is of simple composition. Dolomite with grains of quartz is replaced by galena and chlorite. Locally sphalerite and nickel and copper ores are present.

A slide of a specimen of disseminated lead ore collected by Mr. Franklin Hanley at Mine La Motte was examined by Dr. F. F. Grout. The rounded grains of quartz are cemented by calcite and dolomite. Galena fills spaces between and replaces grains of quartz and carbonate and crosses earlier contacts of carbonate and quartz. Chlorite seems to have the same relations to the

District of Southeastern Missouri, *Eng. and Min. Jour.*, vol. 72, pp. 478–480, 1902; vol. 97, p. 1159, 1914; Keyes, C. R., "A Report on the Mine La Motte Sheet," Mo. Geol. Survey, vol. 9, Rept. No. 4, pp. 1–132, 1895; Pirsson, L. V., "Origin of Certain Ore Deposits," ECON. GEOL., vol. 10, pp. 180–186, 1915.

rock as galena. It cements sand grains and replaces carbonate, and minute veinlets of chlorite cross the earlier minerals. Some

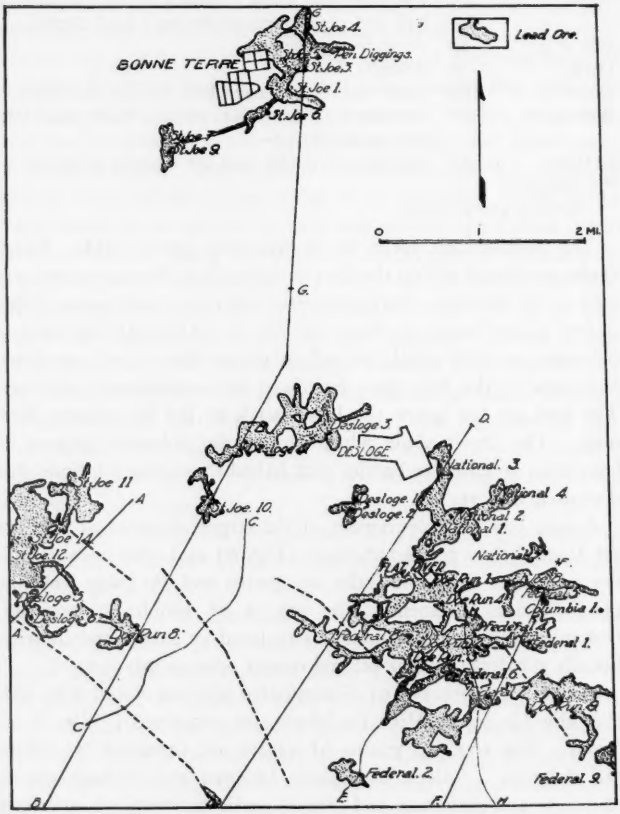

FIG. 5. Plan of the disseminated lead district, Missouri, after Buckley, with additions from company maps.

of the lead ore carries pyrite and small amounts of chalcopyrite. At places the lead ore lies against layers of bituminous shale a

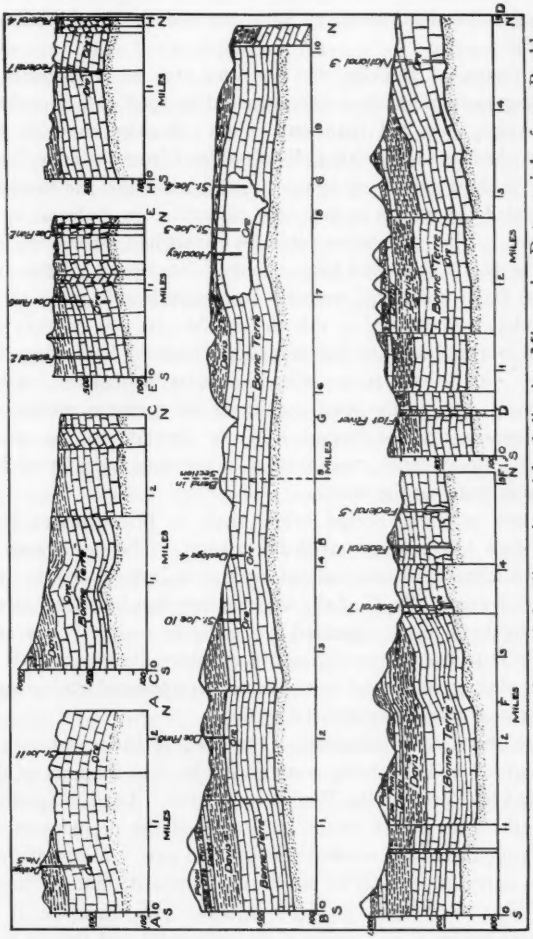

FIG. 6. Geologic cross sections of the disseminated lead district, Missouri. Data mainly from Buckley.

fraction of an inch thick which is found in the Bonneterre limestone, and the shale seems to have favored the precipitation of sulphides.

The theory of Buckley that the lead ores were deposited by ascending meteoric waters was proposed in 1908 and is probably more widely accepted than any other. Buckley assumes that water soaked into the ground, dissolved lead from the rocks below the Davis shale and rising again was checked below the shale and precipitated the metals at and near carbonaceous material in the limestone. This circulation could be established, of course, only after the Davis shale had been removed from parts of the area, and the Davis shale still remains over considerable parts of the area today. According to this theory the ores are of very late age and it would seem to follow that the ores are being deposited to-day. This theory, to me at least, appears inadequate, for lead in ground water is the least mobile of all common metals and these deposits are the largest lead ore deposits in the world. There is little evidence, moreover, of a vigorous transfer of lead by ground water in the mines.

The ore as stated occurs below shale or below places from which shale has been removed by erosion. The occurrence of ore in anticlines and near unconformities is very common. The deposits of practically all of the larger mines that had been opened when Buckley's report appeared are partly or mainly below anticlines or near unconformities and a considerable number of the deposits that were opened since his report appeared are on anticlines or near unconformities (Fig. 6).

Barite Districts of Missouri.—The area of barite deposits of Washington [8] and adjoining counties grades into the area of disseminated lead ores of the Flat River region. Lead is found in nearly all of the barite mines and some of the deposits of the barite group have been worked for lead and zinc. Many of these deposits carry silver and in the Peach Orchard mine in south-

[8] Tarr, W. A., "The Barite Deposits of Missouri," Econ. Geol., vol. 14, pp. 46–67, 1919; Buckley, E. R., "Geology of the Disseminated Lead Deposits of St. Francois and Washington Counties, Missouri," Mo. Bur. Geol. and Mines, vol. 9, pp. 1–259, 1909.

eastern Washington County a deposit near a fault was worked for lead-silver ore some of which contained 30 ounces of silver to the ton. The barite deposits are nearly all residuary ores that have accumulated on an eroded surface of limestone. Barite veins at places are found in the limestone. In the barite district faults are numerous and fissure veins are not uncommon. These veins contain banded ores with barite, quartz, sphalerite and galena and extend northward almost to the Missouri River. The Virginia mine at the north end of this belt worked a vertical baritic vein a mile long to a depth of 480 feet. It was 1 to 15 feet wide and carried a high proportion of lead. In this region one vein followed a slickensided fissure and was worked for lead, zinc and barite.

It is noteworthy that the baritic deposits of Washington County appear in certain beds above the Davis shale at a horizon above the beds that contain the disseminated lead ores near Flat River. The solutions could rise through the shale on account of the extensive faulting and fracturing of the area. Some deep holes have been drilled in this region, but it is said that the cores were not preserved.

Central Missouri Lead District.—The lead-zinc district of Central Missouri lies immediately west of Jefferson City and northwest of the central disc of specularite ores and the ring of pyritic and copper ores that nearly surrounds the central disc. In the central Missouri[9] district small mines are numerous and many of them have been worked but no large deposits are developed. In Miller County zones I, II and III are represented. The geologic section after Ball and Smith is stated below.

Carboniferous		
Coal Measures	0–150′	shale contains some zinc ore and barite.
Unconformity		
Graydon	150′	sandstone.
Saline Creek	60′	cave conglomerate.

[9] Ball, S. H., and Smith, A. F., Mo. Bur. Geol. and Mines, ser. 2, vol. 1, pp. 1–197, 1903; Lee, W., Geology of the Rolla Quadrangle: Mo. Bur. Geol. and Mines, ser. 2, vol. 12, pp. 1–111, 1913; Van Horn, F. B., Mo. Bur. Geol, and Mines, ser. 2, vol. 2, pp. 1–100, 1905; Marbut, C. F., idem, ser. 2, vol. 7, pp. 1–94, 1913.

Unconformity		
Upper Burlington	35′	limestone.
Unconformity		
Cambro-Ordovician		
Pacific	50′	sandstone.
Unconformity		
Jefferson City	200′	dolomite, argillaceous, siliceous, thin layers sandstone and shale; some lead ore in Miller County. Fortuna lead deposits in Moniteau County.
St. Elizabeth	160′	sandstone, dolomite, shale; McMillan diggings with galena and barite.
Gasconade	250′	Limestone, dolomite and chert contains main ores of lead and zinc in Miller County.
Gunter	18′	sandstone; no ore in Miller County.
Procter	57′	limestone; no ore in Miller County.

Ball and Smith attribute the deposition of the ores to ascending waters followed by reconcentration by descending waters.

In Morgan County, northwest of Miller County, lead ores were mined in a circle in Gasconade limestone near the axis of the Proctor anticline. At Bluff Spring in the northern part of the county zinc ore was mined in the Roubidoux formation, which is equivalent to the St. Elizabeth and in the Jefferson City limestone above the Roubidoux. These deposits yielded ore valued at $100,000.

In Moniteau County valuable lead ore deposits have been mined in and near the Fortuna district in the Jefferson City limestone. Although the lead and zinc and barite deposits of the central Missouri district are found chiefly in early Paleozoic rocks they are probably of late Paleozoic age, since some of the deposits are found in shales and coals of the Pennsylvanian, where pockets of the latter appear to occupy ancient sinks.

Joplin Region.—From the central disc of specularite ores southwest to Miami, Oklahoma, ore deposits are closely spaced, as is shown by Fig. 4. The axis of the major zone of deformation of the Mississippi valley which extends west from Kentucky to the central Ozarks, extends southwest beyond the Oklahoma-Arkan-

sas border. The Seneca fault system lies north of this axis in Missouri. A fault of this system has a 700 foot throw. The main Seneca fault which is 80 miles long is not traced east of Mosely in Newton County south of Joplin, where it probably bends to strike more nearly east. A fault and two parallel ore runs strike east at Aurora. The relations of these faults to the

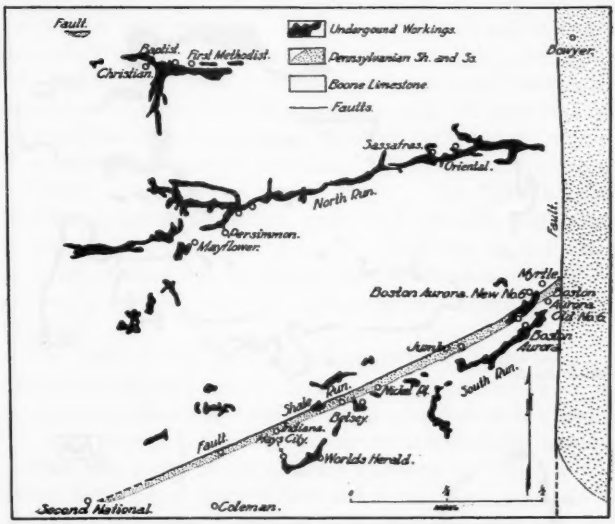

FIG. 7. Plan of Aurora district, Missouri, showing fault system and ore deposits. The deposits are runs parallel to a fault. Data from Bain.

axis of the Ozark uplift and to the zinc deposits of the Joplin region are shown by Fig. 2. East of Aurora the zinc-lead deposits are numerous but relatively small so far as developed. At Aurora,[10] Granby and Joplin, Missouri; Galena, Kansas; and Miami, Oklahoma, are found some of the greatest zinc-lead deposits of the world.

At Aurora (Fig. 7) the zinc deposits lie in a fault that in-

[10] Bain, H. F., Van Hise, C. R., and Adams, G. I., M. S. Geol. Surv. 22nd Ann. Rept., Pt. II, pp. 23–236, 1901.

volves Pennsylvanian and Mississippian strata, and in two runs near and parallel to the fault. Most of the deposits lie 60 to 120 feet deep, but at places the ore is found 500 feet below the surface. Aurora is the chief mining district in Lawrence County which at one time was second in zinc production and third in lead production in Missouri.

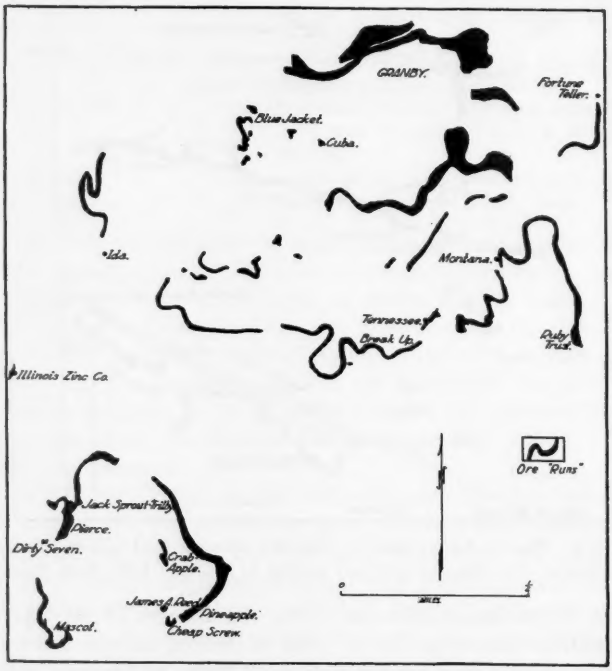

FIG. 8. Map showing runs and circles (black) at Granby, Missouri. These deposits appear to be related to erosion features rather than to faults. Data from Buehler and Buckley.

Granby, 25 miles west of Aurora, is also an important zinc producing district. The deposits (Fig. 8) appear to be related to

ancient erosion channels[11] rather than to faults. The country is Mississippian limestone, mostly flat-lying, below which are 10 to 20 feet of shale, and below that are Cambro-Ordovicion dolomites with chert. The Mississippian limestone is locally covered with Coal Measures shale. After the Mississippian limestone was deposited the country was raised and as shown by Buckley and Buehler the Mississippian was eroded before the Coal Measures shales were deposited on it. Caves were formed and in erosion channels large deposits of chert accumulated. When the country was covered with shale the chert breccias formed channels for metalliferous waters which moved through the openings and cemented the chert breccias and replaced the limestone near by. The deposits are runs or undulating ribbons or cords which are not wide or thick but have great length. The minerals of the deposits are sphalerite, galena, pyrite and marcasite with gangue of chert, calcite, dolomite and quartz. Drill holes in this district at depths of about 600 feet below the upper surface of the Boone showed 6 feet of chert and sphalerite in Cambro-Ordovician limestone.

The Joplin district in southwestern Missouri is the most productive zinc-bearing area in the state. It extends westward into Kansas and Oklahoma[12] and the larger area commonly called the Tri-State district is the most productive zinc-lead district in the world. The rocks of the area are Paleozoic sedimentary rocks nearly flat-lying or gently folded and at places cut by faults and fissures. The main district is on a flat anticline that plunges northwest.

The generalized geologic section, based on data from Moore, Siebenthal, Buehler and others is stated below.

[11] Buckley, E. R., and Buehler, H. A., "The Geology of the Granby Area, Missouri," Mo. Bur. Geol. and Mines, ser. 2, vol. 4, pp. 1–120, 1906.

[12] Bain, H. F., Van Hise, C. R., and Adams, G. I., "Preliminary Report on the Lead and Zinc Deposits of the Ozark Region," U. S. Geol. Survey 22d Ann. Rept., pt. 2, pp. 23–228, 1901; Siebenthal, C. E., "Origin of the Zinc and Lead Deposits of the Joplin Region, Missouri, Kansas and Oklahoma," U. S. Geol. Survey Bull. 606, pp. 1–283, 1915; Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey, Joplin Folio 148, 1907; Winslow, A., Mo. Geol. Survey, vols. 6 and 7, 1895; Bastin, E. S., *Jour. Geol.*, vol. 34, pp. 735–792, 1926.

Pennsylvanian		
Cherokee	0–150′	dark shale and sandstone with a little coal.
Mississippian		
Unconformity		
Carterville	0– 50′	shales and shaly and oolitic limestone; some sandstone.
Unconformity		
Boone formation		contains essentially all the ore mined.
Warsaw	0–150′	cherty limestone.
Short Creek	2– 8′	oolitic limestone.
Keokuk	100′	cherty limestone.
Grand Falls	15–120′	heavily bedded chert, "sheet ground."
Burlington	100–150′	limestone, cherty, shaly partings.
Northview	0– 20′	shale; practically no ore mined below it in Joplin district.
Ordovician		
Jefferson City	500′ ±	dolomite.

The rocks below the Boone chert are not exposed in the Joplin district, but the Harrington well at Carthage shows the following section, correlated by Ulrich. This section is reported in the Joplin Folio.

Mississippian	
Burlington and Keokuk limestone (Boone)	355′
Chouteau limestone	15
Hannibal shale	15
Louisiana limestone	65
Ordovician	
Joachim limestone	50
St. Peter sandstone	85
Cambro-Ordovician and Cambrian	
Limestones and sandstones	1165
Pre-Cambrian	
Porphyry	255

The Hannibal shale, 15 feet thick, is the only shale member between the pre-Cambrian and the rocks containing the ore. Above the limestone containing the ores there are thick shales.

The ore deposits are included in Zone III. They are chiefly in the Boone formation of the Mississippian system, although some ore is found in Pennsylvanian rocks. The ores are in runs, circles and sheet ground, and certain deposits are in "crevices" although there are no well defined fissure veins. The "run" is a long narrow body of ore generally shallow and commonly flat-lying or inclined at low angles. It is in disturbed and often brecciated strata, slickensided and marked by minor faulting. Two parallel single runs are often connected by cross runs to form a long compound run. The Arkansas run at Belleville, Missouri, is over one quarter mile long. Certain runs are at places 300 feet wide but they are generally from 10 to 50 feet wide; their vertical extent is about the same but some locally reach 150 feet. Some of the runs bend and others make complicated curves. Circles are elliptical closed or nearly closed runs. They are numerous and widespread. They vary in size from 100 feet to about 1,300 feet in diameter.

The ore deposits, as stated, are chiefly in the Boone formation. Nearly all of the ore is in chert. Extensive beds of white chert of the Boone formation were brecciated and the fragments are cemented by dark chert and ore. There was silicification of the Boone limestone at an early stage, but no black chert was formed and little or no ore. Bitumen and oil are associated with the ore and the black chert owes its color to oily matter presumably of Pennsylvanian age. The minerals of the deposits include sphalerite, galena, pyrite, marcasite, chalcopyrite, and greenockite, with a gangue of chert, calcite, dolomite, and crystalline quartz. The quartz is not abundant, and I have observed no rose quartz or purple quartz like that of the central specularite disc of Zone I. Barite is not abundant but is noted in several deposits.

As shown by Fig. 4, metalliferous deposits are closely spaced from the central Ozark region to the Joplin district. There is a group of scattered deposits near Carthage, northeast of Webb City. In the main ore bearing area of the Joplin district (Fig. 9), there are 4 belts of ore bearing ground that strike northwest. One passes through Webb City, another through East Joplin, a

third through the western part of Joplin and a fourth further west extends from Belleville to Tanyard. These belts are marked by numerous patches of coal measures strata that have not been eroded from the Boone limestone that underlies nearly all of the area.

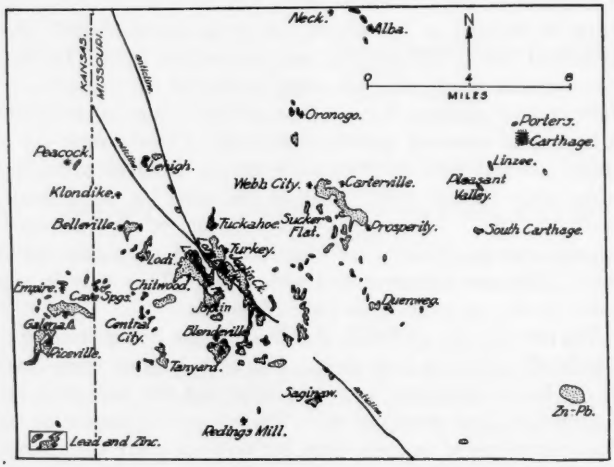

FIG. 9. Map of Joplin region, Missouri, showing chief mining districts. Data from Siebenthal, Smith, Bain, Adams and others.

In the Carthage area on the northeast edge of the district deposits of zinc and lead are opened at Porters mine on the northwest edge of Carthage near Spring River where the ores are found in chert and limestone breccia below Pennsylvanian shale. Similar relations exist at the Linzee mine southwest of Carthage. Barite, which is rare in this region, has been found in the Carthage mines. At Pleasant Valley 3 miles southwest of the deposits at Carthage the Cornell shaft 143 feet deep passed through 50 feet of soil and shale, then 15 feet of limestone below which was 80 feet of clay, chert and limestone breccia, the lower 15 feet of which was ore bearing.[13] In adjoining workings there was a

[13] Winslow, A., *op. cit.*, p. 591; Bain, H. F., *op. cit.*, p. 184.

very wide face of ore. According to Bain there is a considerable fault in this area. Some of the ore occurs as sheets between beds of unbroken limestone and chert. At South Carthage 2 miles south of Pleasant Valley the ores are associated with the Pennsylvanian strata.

The east belt is 10 miles long and extends from Oronogo southeast through Webb City to Duenweg. At the north end of this belt, at Oronogo, valuable deposits of zinc and lead opened at an early date were described by Swallow in 1854. The Oronogo circle is a topographic depression containing an ancient sink hole into which the beds dip from the slides. It is about 800 feet in diameter, and 200 feet deep or more, the ore extending down to the sheet ground of the Grand Falls chert. Around the margin of the sink was a ring of the ore 50 to 100 feet wide and 30 feet thick or more. The ore is a white chert cemented by dark chert containing much sphalerite. The circle is evidently a pre-Pennsylvanian sink hole, since it is partly filled with shales and coal. Bain states that it is crossed by faults and evidently it has been deformed in post-Pennsylvanian time since it contains many fragments of chert and limestone and bits of coal of Pennsylvanian age. Other circles are developed in Center Creek valley between Webb City and Carterville and on the Missouri Zinc Fields land at Webb City. At Sucker Flat, adjoining Webb City to the south, an ore-bearing area about a half mile long nearly coincides with an outcrop of Cherokee shale. The ore-bearing area occupies a syncline or sunken area showing dips of 45° to 90° around the margin.

The Webb City belt contains extensive areas of "sheet ground." Such deposits are blanket veins nearly horizontal and of great lateral extent. These ores follow the bedding and are commonly developed at the top of the Grand Falls chert 100 feet below the Short Creek oölite. In this ground the white chert is very extensively brecciated and cemented with dark chert containing sphalerite and galena. The brecciation is due to movement of beds along the bedding and to solution of limestone followed by collapse of the chert. These nearly horizontal sheets of

ore are commonly over a thousand feet long, several hundred feet wide and 10 feet to 30 feet thick. Great bodies of sheet ground are developed between Webb City and Prosperity and with interruptions southwest of Prosperity to Duenweg. Northwest of Webb City it is found as far as Oronogo.

The Cornfield bar is about 1 mile southeast of Webb City. A "bar" marks an abrupt change from ore to poor or barren ground along a nearly horizontal plane. In this region[14] there is a great block of sheet ground at a depth of about 170 feet. It is developed in the Boone chert and is 2,000 feet long, 400 to 800 feet wide and has a face about 10 feet high. Through this area runs a barren bar 50 to 300 feet wide in which the ground is broken and confused. The rocks dip toward this bar. The sheet ground is poor in the bar but rich on either side of it. The middle of the bar carries broken shale and chunks of coal. The mass is highly fractured. The confused Coal Measures rocks lie at places 185 feet below the surface of the Boone and the relations have been interpreted as indicating a graben with that amount of displacement. Extensive developments underground, however, have shown that in the main the position of the body of Coal Measures rock is due to deposition unconformably in a pre-Pennsylvanian erosion trough, at which time surface channels, sink holes and cave galleries were filled with Coal Measures rocks. Later these filled channels, which constituted lines of weakness, were deformed by the pressures which threw the rocks of the area into gentle folds. This deformation caused further brecciation and solution. The faults of the area, according to Siebenthal, have throws probably not more than 25 or 30 feet rather than 100 or 200 feet as would be indicated by the present positions of the rocks.

The East Joplin belt contains the mining areas of Tuckahoe, Turkey, Lone Elm Hollow, Joplin Creek, and extends southeast to Saginaw. The west belt extends from Lehigh through Chitwood, Blendville and the area near Redings Mill. The Central City belt strikes northwest and includes Belleville, Lodi and

[14] Siebenthal, C. E., "Structural Features of the Joplin District," ECON. GEOL., vol. 1, pp. 119–128, 1905.

Central City and Tanyard. The Neck-Alba belt north of Webb City is a short belt that strikes northwest. The Galena belt strikes southwest and includes Cave Springs, Empire, Galena and Riceville. This belt is parallel to the Seneca fault belt that lies to the south. In the Miami district, Oklahoma, certain runs of ore trend northwest parallel to the ore belts of Joplin and others trend northeast parallel to the belt of Galena, Kansas, and to the Seneca fault system. There is thus a rude conjugation of runs or belts of deformation, which suggests compressive stresses. There are faults of the Seneca group that have throws of several

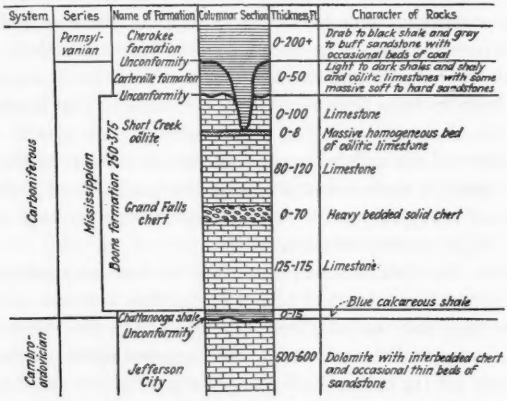

FIG. 10. Generalized section of Joplin region. Data from Siebenthal, Naething and others.

hundred feet and one has a throw of 700 feet. It appears probable that there are faults in the Joplin district of sufficient magnitude to displace any shales that lie below the ore bodies sufficiently to allow metallizing solutions to rise to the region of the brecciated Boone formation. When the ore was deposited it is probable that the Pennsylvanian shale capped the Boone formation over most of the district and served as a barrier to rising waters that deposited the ore in brecciated chert beds and in ancient

solution breccias and caves. A section of the area is shown by Figure 10.

The Miami [15] district in northeastern Oklahoma extends across the state line into Kansas. It is a subdistrict of the greater Joplin or Tri-State district and is the most important zinc producing area in the United States. The surface of the country is nearly flat and it is underlain by gently folded sedimentary rocks. A large area is covered over by an unbroken bed of Cherokee shale 50 to 200 feet thick, which rests on an eroded surface of Boone limestone. This situation contrasts with the mining camps around Joplin where the shale is eroded except for depressions in the underlying limestone. In Oklahoma the ore bodies are wide irregular blankets or broad "runs" below the shale and lie in both the troughs and at high places on the pre-shale surface. They seem to have little relation to the folds. The blankets are generally elongated and the longer axis of one system strikes northeast and the axis of another strikes northwest so that there is, as stated, a rude conjugation in the plans of such deposits. There are many important deposits which seem to have no relation to either system of runs.

Before the shale was deposited the surface was subjected to long continued erosion and bodies of solution breccias, sink holes and probably cave systems were developed as in the Joplin region. These features of the ancient surface supplied openings that were favorable for the entrance of rising waters and for the deposition of ores. A great trough or zone of deformation known as the Miami fault, strikes northeast through the Commerce district.[16] This is ascertained by great disturbances of the beds and by slickensided surfaces. It has been regarded as a fault although according to Siebenthal it may have developed mainly as a result of

[15] Siebenthal, C. E., Contour map of the surface of the beds underlying the Cherokee shale in a portion of the Pitcher district, Oklahoma, issued with a 4-page Press Bulletin by the U. S. Geol. Survey, April 20, 1925; Weidman, S., Tri-State lead and zinc district: Okla. Bur. of Geol., p. 19, April 1925; Naething, F. S., "The Oklahoma, Kansas, Missouri Zinc-Lead Field," *Eng. and Min. Jour.*, vol. 122, pp. 604–608, 1926.

[16] Heap, R. R., "A Geological Drainage Problem," *Eng. and Min. Jour.*, vol. 96, pp. 1205–1211, 1913.

solution similar to that already noted by Siebenthal in the Cornfield Bar. It is noteworthy, however, that this fault is nearly parallel to the Seneca fault in Oklahoma, which lies a short distance to the south. Naething states that the Miami fault is chiefly a pre-Carterville erosion channel possibly controlled by pre-Carterville faulting, which was subsequently a line of weakness, and that a small amount of faulting not to exceed 50 feet may have occurred along it since deposition of the Pennsylvanian.

A section of the rocks after Siebenthal is shown as Fig. 10. The granite is probably 1,000 to 1,500 feet below the surface. The Chattanooga shale is from 0 to 15 feet thick. It appears probable that even minor faulting would permit rising solutions to pass through the shale.

The Miami ore bodies are at horizons between beds 50 feet above the Short Creek oölite and the bottom of the Grand Falls chert. The ores are sphalerite, galena, marcasite, chert and dolomite. Nearly all of the ore is in brecciated white or pink chert although a little is in limestone. There is a rude vertical zoning and the upper and outer parts of an ore body generally contain more lead than the bottom and central parts.

According to Siebenthal[17] there are considerable areas in the Joplin region which are underlain by thick Chattanooga shale; in such areas large deposits of ore have not been discovered. Over most of the mineral-bearing area the Chattanooga shale appears to be thin or wanting or discontinuous.

In Okfuskee County, Oklahoma, copper ore is found in a fault zone cutting reddish and greenish sandstone of either Upper Pennsylvania or Lower Permian age (Fig. 2). The ore consists of angular quartz grains, corroded around their edges, probably by mineralizing solutions, which are cemented by malachite and limonite and small bodies of tetrahedrite[18] occur in the malachite.

Northern Arkansas.—Zone III extends southward from Missouri into northern Arkansas where zinc and lead deposits are

[17] Siebenthal, C. E., "Origin of the Zinc and Lead Deposits of the Joplin Region," U. S. Geol. Survey Bull. 606, pp. 200–202, 1915.

[18] Foley, L. L., Written communication. Tetrahedrite identified by Dr. G. M. Brownell.

found over a large area. Transportation facilities are poor and the deposits are not greatly developed. The rocks dip at low angles but are extensively faulted, one fault being mapped 7 miles on strike. The rocks are shown in the following section.

Pennsylvanian		
Winslow		sandstone and shale
Morrow		shale
Unconformity		
Mississippian		
Pitkin	10′– 40′	limestone
Fayetteville	50′–200′	shale, black carbonaceous
Batesville	75′ ±	sandstone
Boone	325′	limestone, cherty, ore horizons; St. Joe member of Boone is an even bedded limestone up to 50 feet thick, free from chert; contains no ore
Noel	0′– 70′	shale, seldom contains ore
Unconformity		
Devonian		
Sylamore	40′ ±	sandstone, some shale, phosphate pebbles
Unconformity		
Ordovician		
Polk Bayou	15′ ±	limestone, seldom contains ore
Izard	0′–240′	limestone
Key	1′– 10′	sandstone
Yellville		very thick limestone, cherty, contains chief ore deposits

The ore is found chiefly in flat lying brecciated zones of chert in the Yellville and Boone limestones. A considerable number of the deposits are along faults although the ores are not in the actual planes of the faults. The zones of brecciated chert and limestone are due in part to movement along bedding planes. The north Arkansas mineralized area does not extend southward to the Ouchita Mountains but is separated from the latter by an area about 75 miles wide in which there are no deposits of sulphide ores. The zinc-lead ore belt extends eastward, however, to near the Mississippi embayment where it lies between the belt of iron ore on the north and the Batesville manganese district on the south. The iron ores as already stated are in the south ex-

tension of Zone II which is extensively developed in Missouri. The iron ores and also the zinc ores cement chert breccia.

Batesville district.—The Batesville[19] manganese district is about 85 miles long and lies south of the zinc district. The district produced 159,000 tons of ore prior to 1921. The country is an area of Paleozoic sedimentary rocks that dip at low angles. The section after Miser is as follows:

Section of Batesville district, Arkansas. After H. D. Miser.

Mississippian		
Batesville	20′–200′	sandstone.
Moorefield	100′–250′	shale.
Boone	300′–400′	chert, limestone.
Unconformity		
Devonian		
Chattanooga	0′– 38′	shale.
Unconformity		
Penters	0′– 91′	chert.
Unconformity		
Silurian		
Lafferty	0′– 85′	limestone.
St. Clair	0′–100′	limestone.
Brassfield	0′–?	limestone, very thin.
Ordovician		
Cason	0′– 13′	shale with limestone nodules, sandstone, phosphatic rock; manganese ore (carbonates and oxides).
Fernvale	0′–125′	limestone; upper part contains manganese deposits (carbonates and oxides).
Unconformity		
Kimmswick	12′– 55′	limestone.
Unconformity		
Plattin	128′–240′	limestone.
Unconformity		
Joachim	20′–150′	limestone.
St. Peter	120′–200′	sandstone.
Unconformity		
Magnesian	1650′+	limestone and sandstone.

These rocks are thrown into folds and faulted. The ore deposits as stated by Miser, are manganese carbonate ore enriched by

[19] Miser, H. D., deposits of manganese ore in the Batesville district, Arkansas: U. S. Geol. Survey Bull. 734, pp. 1–273, 1922; Penrose, R. A. F., Jr., Ark. Geol. Survey Ann. Rept., vol. 1, 1891.

oxidation to form manganese oxides. The lowest shale noted in the section is the Cason shale which is composed of shale with limestone nodules, sandstone and sandy phosphatic rock. The manganese carbonate ore is found in the Fernvale limestone below the Cason and replacing the limestone nodules and fossils in the Cason shale. The ore contains barite, a little fluorite and at places a little galena and pyrite. Arsenic and copper are identified in some of the ores.

The Cason mine near Batesville, which has produced about 40 per cent of the ore marketed, is located not far from the crest of a broad anticline. The ore is in the Cason shale, which includes numerous buttons an inch in diameter or less. These are nodules, mainly calcareous aggregates of algae, which have been replaced by manganese carbonate and later oxidized by weathering. Small veins of mangano-calcite and barite cut the Cason shale. Galena, pyrite, and arsenopyrite are found at the mine. In the Grubb Cut mine and in certain other mines of the area the ore is residuary clay that accumulated on an ancient erosion surface near the top of the Fernvale limestone and below the Boone chert. The Cason shale is eroded. The Boone limestone carries little manganese where the Cason shale was eroded before it was laid down. Residuary clay at the base of the Boone would probably serve as effectively for barriers to rising waters as the Cason shale where it was present.

This district is tentatively placed in the zonal series as Zone IV. It should be stated, however, that the vertical range of manganese carbonate in mineral deposits is so great that the mineral has little significance for or against the hypothesis that the Batesville ores are zoned with the ores of the Ozark region.

Illinois-Kentucky Fluorspar District.—In southern Illinois and western Kentucky deposits of fluorspar are mined, together with ores of lead and zinc. The production of fluorite exceeds that of any other district in the world. The country [20] is an area of

[20] Bain, H. F., U. S. Geol. Survey Bull. 255, pp. 1–75, 1915; Weller, S., Butts, C., Currier, L. W., and Salisbury, R. D., Ill. Geol. Survey Bull. 41, pp. 1–416, 1920; Currier, L. W., Fluorspar deposits of Kentucky: Ky. Geol. Survey, ser. 6,

Devonian and Carboniferous rocks which are exposed around a sharp domatic uplift that is extensively faulted on its southeast side. The chief faults strike northeast and contain the chief ore deposits. Igneous dikes are exposed at 7 places in Illinois and at many places in western Kentucky. Most of the dikes are peri-

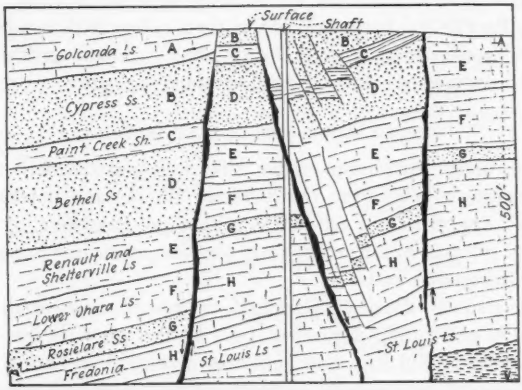

FIG. 11. Generalized geologic cross section showing Rosiclare vein, Blue Diggings shaft, after Weller.

dotite although an acid breccia is exposed 2 miles northwest of Rosiclare, Illinois. The deposits are chiefly veins that occupy fault fissures that lie nearly vertical or dip at high angles and displace Mississippian limestone. The Rosiclaire-Fairview vein (Fig. 11) is developed a mile on strike and to a depth of 725 feet. It is from 6 to 30 feet wide. It is a banded deposit and contains the largest fluorspar deposits in the district. The minerals besides fluorite are: calcite, barite, quartz, sphalerite, galena, pyrite and chalcopyrite. The galena is concentrated in the upper part of the vein and sphalerite below. Near the surface galena makes up 2 per cent of the vein but below 200 feet galena disappears

vol. 13, pp. 151–168, 1923; Spurr, J. E., *Eng. and Min. Jour.*, vol. 122, p. 751, 1926; Fay, A. H., *Eng. and Min. Jour.*, vol. 122, pp. 165–169, 1926; Bastin, E. S., report in preparation.

and sphalerite is the chief sulphide. The sulphides are intergrown with fluorite and are primary. Numerous other veins from 2 to 6 feet wide or more are found in the district. Bastin has shown that the veins are, in part, replacements.

At Cave-in-Rock and at Lead Hill 4 miles northwest of Cave-in-Rock several veins are found lying with the bedding. They carry fluorite and barite and one of them 4 feet thick is a bedding plane deposit lying directly below shale. Small vertical veins extend downward below the bedding plane deposits.

UPPER MISSISSIPPI VALLEY DISTRICT.

The upper Mississippi valley zinc and lead district[21] lies in southwestern Wisconsin, northwestern Illinois and northeastern Iowa. The district is estimated to have produced 611, 975 tons of lead to 1904, but in recent years the zinc production has greatly exceeded that of lead.

The rocks of the district are early Paleozoic sedimentary rocks which in general dip southwest about 15 feet per mile, but which are locally folded into low anticlines and shallow basins. The rocks are cut by hundreds of fractures or "crevices" which are metal bearing and in many parts of the district constitute the

[21] Owen, D. D., Rept. Geol. Survey Wisconsin, Iowa, and Minnesota, pp. 1–638, Philadelphia 1852; Whitney, J. D., Geol. Survey Iowa, vol. 1, pp. 422–471, 1858; Whitney, J. D., "Metallic Wealth of the United States," pp. 403–417, 1854; Percival, J. G., Ann. Rept. Geol. Survey of Wis., pp. 7–101, 1855; Strong, M., "Geology and Topography of the Lead Region," Geol. Survey Wis., vol. 2, pp. 643–752, 1877; Chamberlin, T. C., "The Ore Deposits of Southwestern Wisconsin," Geol. Survey Wis., vol. 4, pp. 365–571, 1882; Jenney, W. P., "Lead and Zinc Deposits of the Mississippi Valley," *Amer. Inst. Min. Eng. Trans.*, vol. 22, pp. 171–225, 621–647, 1893; Blake, W. P., *Amer. Inst. Min. Eng. Trans.*, vol 22, pp. 558–568, 1894; also *Amer. Geol.*, vol. 12, pp. 237–248, 1894; Leonard, A. G., "Origin of the Iowa Lead and Zinc Deposits," *Amer. Geol.*, vol. 16, pp. 288–294, 1895; Calvin, S., and Bain, H. F., "Geology of Dubuque County," Iowa. Geol. Survey, vol. 10, pp. 379–622, 1900; Grant. U. S., Lead and Zinc Deposits of Wisconsin, Wis. Geol. Survey Bull. 14, pp. 1–100, with atlas, 1906; Ellis, E. E., Zinc and Lead Mines near Dodgeville, Wisconsin," U. S. Geol. Survey Bull. 260, pp. 311–315, 1904; Bain, H. F., "Zinc and Lead Deposits of the Upper Mississippi Valley," U. S. Geol. Survey Bull. 294, pp. 1–151, 1906; Cox, G. H., "Lead and Zinc Deposits of Southwestern Illinois," Ill. Geol. Survey Bull. 21, pp. 1–120, 1914; Spurr, J. E., "Upper Mississippi Lead and Zinc Ores," *Eng. and Min. Jour.*, vol. 117, pp. 246–250, 287–292, 1924.

chief mineral deposits. No igneous rocks are found within the area and it is generally stated that there are no faults with more than a few inches of throw. There are great differences of opinion regarding the amount of faulting within the area. The

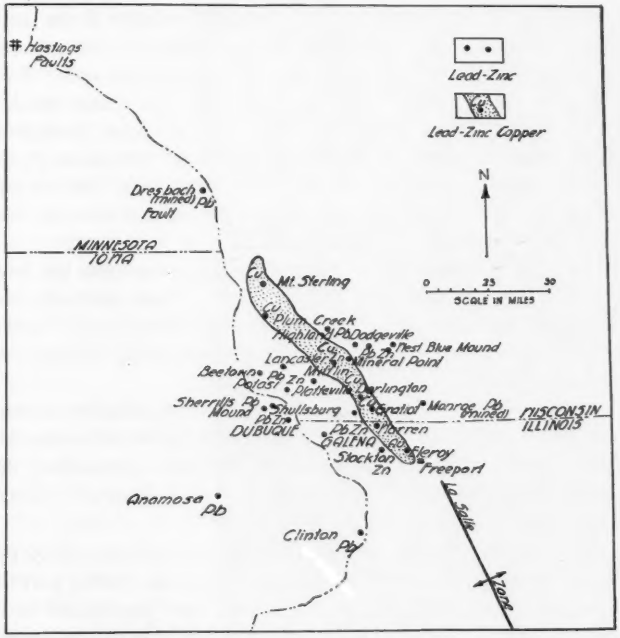

FIG. 12. Plan of Wisconsin, Ilinois and Iowa lead and zinc district, showing mineral zones and their relations to the LaSalle zone of deformation.

most detailed structural maps that have been made in the area, however, show practically no faulting. As shown by Fig. 12 the LaSalle anticline which is followed about 300 miles in Illinois strikes northwest and if continued would pass into the district. This persistent zone of deformation is not known north of

Illinois, but a fault with considerable displacement is found at Dresbach, Minnesota. At Hastings, Minnesota, faults with about 100 feet throw displace the Ordovician rocks and in northern Washington County about 40 miles north of Hastings [22] a fault mosaic is found in rocks of the same system. These places would be almost in line with the LaSalle anticline if the latter were produced. At least they show that faulting is not unknown in the upper Mississippi valley near the mineralized area. Near Meekers Grove, Wisconsin, the rocks show a sharp anticline striking northwest. If this is on the LaSalle zone it suggests that the latter curves to the west and does not pass through the mining district to the northwest. This seems to be the interpretation of the fold that is suggested by a generalized structure map of T. C. Chamberlin that was published at an early date.

Jenney and Blake reported faulting within the area, but later investigators question their interpretations. Bain states that the faulting reported by Blake to be shown near Shullsburg, Wisconsin, is probably due to irregular dolomitization in the Galena limestone.

Jenney, and later Spurr, suggest that horizontal faults are present and Spurr notes that limestone lentils in the oil rocks are brecciated and that the oil shale forms a paste surrounding the fragments of limestone. Bain notes horizontal striae in a Platteville mine.

A geologic section of the area is shown in column 1, Fig. 14. It is noteworthy that the "flint beds" are in the middle part of the Galena formation, that the "oil rock" or "clay seam" is at its base, and that the "glass rock" is near the top of the Platteville formation.

The ores are found in all rocks from the Niagaran dolomite to the Cambrian sandstone. The occurrences in the Niagaran dolomite are of little importance though galena is found at Sherrill Mound in Jefferson Township northwest of Dubuque, and attempts have been made to mine galena ore from the Niagaran at

[22] Stauffer, C. R., personal communication; Peterson, Eunice, "Block Faulting in the St. Croix Valley," *Jour. Geol.*, vol. 35, pp. 368–374, 1927.

Clinton, 50 miles southeast of Dubuque, and at Anamosa 35 miles southwest of Dubuque. Sphalerite and galena with barite are found in the Maquoketa shale and the Glanville prospect at Scales Mound, Illinois, 10 miles northeast of Galena has opened a deposit in thin dolomite bands in the Maquoketa shale. Ore occurs at all horizons in the Galena formation. In the Dubuque area the ore is in crevices and the bulk of the ore came from places where the vertical crevices crossed a favorable bed 40 feet below the Maquoketa shale and pipes of ore extended along crevices up to the shale. In Wisconsin and in Illinois the middle and lower beds of the Galena are the most productive. The oil rock at the base of the Galena is a bituminous shale and gases from it are believed to have caused the precipitation of the ore. It weathers to form clay. The Galena limestone is largely eroded from the east part of the district and there the Platteville formation produces considerable ore which is largely found in the "glass rocks" or brittle limestone of the Platteville. Ore is found also in limestone beds below the glass rock. Recently considerable ore has been found in the western part of the Wisconsin area in the Platteville limestone below the clay bed which marks the base of the Galena. A little galena is found near the top of the St. Peter sandstone and considerable ore has been mined from the Prairie du Chien dolomite.

The deposits occur in "crevices," in flats and pitches, and as disseminated ore in shaly beds. The crevices are persistent and many of them are followed two miles on strike. The ore is generally in "openings" or "runs" at places where the crevice crosses favorable beds. In the flats and pitches the ore follows flat beds and inclined crevices stepping from one to the other. At places crevices pass downward into flats from which the ore pitches in all directions. The system has the plan of a long ellipse and the pitches commonly join a wide flat near the bottom of the deposit, the shape of the whole deposit being roughly that of a domestic flatiron. Such a system of openings as shown by Grant is often found in a shallow basin just above the oil rock, and is believed to have resulted from collapse due to shrinkage of the oil rock.

Often the fissures are seen to end at clay beds or shales at the top or bottom of the Galena limestone. It has been suggested by Spurr that this is due to horizontal faulting. Striae indicating such movement in the Empire mine at Platteville are noted by Bain.

At places sphalerite and galena are disseminated in strata that contain beds of clay or shale. These deposits are "flats" and some of them are of considerable extent. Such ore is found at Dugdale mine, 3 miles west of Platteville. In the Gruno [23] mine in the Mifflin district a flat which is ore-bearing in the Galena limestone is joined by ore that passes through the oil shale where the ore is disseminated and into the glass rock below the oil shale where also it is ore-bearing (Fig. 13).

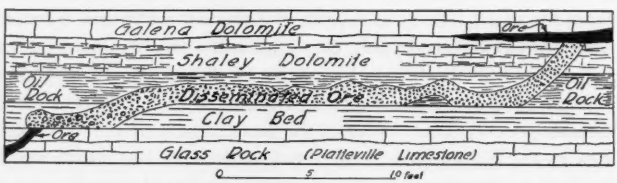

FIG. 13. Cross section of Gruno Mine, Wisconsin, showing ore passing through the oil rock and clay bed. (After Bain.)

Zoning of Ores.—Where lead and zinc are found in the same system of deposits lead is generally more abundant in the upper parts of the deposits and zinc in the lower parts. In some of the mines now worked for zinc there is very little lead. This relation is due partly to the leaching of zinc, which is more soluble than lead in ground water, but as stated by Bain there are reasons for supposing that lead was originally more abundant than zinc in upper beds and zinc more abundant below.

There is a rude horizontal zoning also, in that copper ores and gold are found in a belt that strikes northwest on either side of which are lead and zinc ores without appreciable copper. This belt lies approximately in the strike of the LaSalle zone of de-

[23] Bain, H. F., *op. cit.*, p. 100.

formation and, if continued, would include the copper mines once worked on Plum Creek and at Mount Sterling, Wisconsin.

The Copper-Gold-Zinc-Lead Zone.—In Stephenson County, on the north end of Erin Mound, just west of the village of Eleroy, 35 miles east of Galena, gold occurs in certain beds of Maquoketa shale about 12 feet above the top of the Galena limestone. The Galena and overlying shale carry thin layers of ore with sphalerite, galena, pyrite and native copper. A shaft sunk on a thin crevice encountered the gold-bearing layer at a depth of 20 feet. The gold is associated with rose quartz and small fragments are said to carry 4 ounces of gold per ton.[24]

Native copper is found near Gratiot, Wisconsin, and deposits of copper ore have been prospected at several places between Gratiot and Mineral Point. About 1 mile northeast of Mineral Point Court House oxidized copper ore was mined between 1837 and 1875. More than 2,000,000 pounds of copper were recovered [25] valued at about $500,000.

About 40 miles northwest of Mineral Point and northwest of the zinc district, at the Plum Creek copper mine, in the valley of Plum Creek, a tributary of the Kickapoo river, copper ore was mined in the Lower Magnesian limestone about 150 feet above the top of the Cambrian sandstone. The ore is malachite and is found in small veins and pockets. Two car loads of ore were shipped. About 12 miles north of Plum Creek mine and a mile southwest of Mount Sterling [26] village copper ore was mined from the Lower Magnesian limestone.

Zinc and Lead Zone.—The Mineral Point district has yielded large amounts of lead and zinc ore besides the copper ore already noted. Since the St. Peter sandstone crops out along streams in the district, the lead and zinc ores are above the water table. This encouraged their early mining [27] and not much is known of

[24] Hershey, O. H., "The Gold Bearing Formation of Stephenson County, Illinois," *Amer. Geol.*, vol. 24, pp. 240–244, 1899.

[25] Cox, G. H., Bull. 21 Ill. Geol. Survey, p. 89, 1914; Strong, M., "Copper in the Lead Region," Wis. Geol. Survey, vol. 2, pp. 741–742, 1877.

[26] Strong, M., Wis. Geol. Survey, vol. 4, pp. 69–71.

[27] Strong, M., Geology of Wisconsin, vol. 2, pp. 733–738, 1877.

the character of the deposits. The ore is mined near the base of the Galena limestone and in the glass rock of the Platteville limestone.

The Dodgeville district is in the northeast part of the mineralized area. The country is eroded so that at most places only 50 to 100 feet of Galena limestone remain. The base of the Galena formation is marked by a shale bed 1 to 3 feet thick, which consists of blue clay and "oil rock." Below the latter the Platteville limestone is found. A section of the Dodgeville district after Ellis is given below.

Galena	
Flinty limestone	100′
Limestone without flint	50′
Clay bed (oil rock)	1′–3′
Platteville	
Glass rock with main ore beds (limestone)	10′
Carbonaceous shale	0′–3″
Hard gray limestone	10′
Fossiliferous limestone	18′
Clay bed	0′–2″
Dolomitic limestone	25′
Sandy shale	0′–8″

The deposits include lead and zinc ores which are mined in vertical and in pitching crevices and in large flats. Little ore is found in the Galena limestone, most of it being concentrated in the glass rock of the Platteville limestone. This ore lies in irregular flats from which small veins extend upward. The main ore body is 60 feet wide and 1 to 7 feet thick and extends irregularly in length for a considerable distance. Galena ore is found also in the upper part of the Prairie du Chien limestone.

In the Linden district, northwest of Mineral Point, a narrow structural basin crosses the district, its axis striking east. On it are developed the Mason, Glanville and Milwaukee mines. Crevice deposits yielded lead ore, and below them zinc ore with some lead is found in flats and pitches. The Mason mine worked crevices in the flint rock and a great flat, shaped like the letter J, with the long arm a half mile long extended northwest. Valu-

able zinc deposits were developed at the glass rock horizon, the main flat lying only 20 feet above the St. Peter sandstone.

In the Highland district 10 miles northwest of Linden, the ore is found disseminated in the oil rock and in the glass rock immediately below the oil rock. In the Mifflin district west of Mineral Point, deposits with flats and pitches are worked in several mines. In the Gruno mine a body of zinc ore passes from the Galena limestone into the glass rock through 5 feet of oil rock and clay.

The Platteville district contains several of the largest zinc mines in Wisconsin. Valuable deposits with flats and pitches are worked in the lower part of the Galena limestone above the oil rock. In the upper part of the Empire mine striae record horizontal movement of beds. In the Potosi district, 12 miles southwest of Platteville, the rocks are very gently warped and a small thrust fault is noted. The ore worked is found in the Galena limestone and in certain mines it lies just above the oil rock. In other mines it lies some distance above the oil rock. Near Beetown and Diamond Grove some 12 miles northwest of Potosi crevice deposits are found. The Hazel Green district is about 12 miles south of Platteville. A considerable ore-bearing area extends east through Benton and New Diggings to Shullsburg. At the Hazel Green mine 1 mile northeast of Hazel Green is an area of parallel crevices that strike east and pass downward into the cherty beds of the Galena. The Kennedy[28] crevice at a depth of 63 feet widens into a long narrow opening with crevices pitching outward on both sides forming a considerable orebody.

In the Mills Diggings, the Hoskins and Kennedy mines east of Hazel Green, typical flats and pitches are developed in the Galena limestone above the oil rock, the ore extending upward into the flint beds or cherty layers of the Galena. The ore is chiefly in the flats and pitches, not much of it being disseminated in the area between them. In the Empress mine 2 miles north of New Diggings, flats and pitches in and just above the oil rock are

[28] Grant, U. S., *op. cit.*, p. 66, 1906.

worked. In the Meekers Grove district north of Benton the rocks are folded and at places dip 5° to 10°. The main deposits are runs of ore in the Galena limestone on the north side of an anticline near its crest. In the Shullsburg district there is a pronounced monoclinal dip to the south-south-west. The ore is at the bottom of the Galena limestone and at the top of the Platteville and is much brecciated.

In the Galena district in northwest Jo Davies County, northwestern Illinois, numerous deposits were worked near Galena at an early date and later the Vinegar Hill district was reopened north of Galena. The Vinegar Hill mine was opened in 1904 on an east-west crevice [29] cut by a crevice striking east of north. The crevices were worked for lead ore near the top of the Galena limestone. In depth they join and form an ore body shaped like a horseshoe with flats and pitches between which in the lower part of the Galena limestone is found a mineralized core of workable ore which yields sphalerite with a little galena.

In the Elizabeth district 12 miles southeast of Galena the rocks cropping out include the Galena limestone and Maquoketa shale. The Wishon mine works a long east-west crevice; the chief ore is in and above the flint beds. Pitches and fractures dip away from the Crevice into the flint beds north and south. The area between them is mined leaving open drifts 150 feet wide and 50 feet high.

Illinois mine a mile southwest of Elizabeth worked an area with crevices striking east cut by other crevices striking north.

The Skene [30] mine a mile south of the Illinois mine, is on an east-west crevice which at 96 feet deep branches into "two pitches." The deposits yielded about 4,000,000 pounds of lead ore which came from the upper part of the Galena limestone.

The Royal Princess or California mine is in the Sand Prairie district near the Mississippi river at the extreme south edge of the district in a ravine which cuts back into the Niagara escarpment. This ravine parallels the vein which strikes east and is opened by an adit driven 2350 feet. The beds dip at a low angle.

[29] Cox, G. H., *op. cit.*, pp. 49–51.

[30] *Idem*, p. 59.

The main workings are the drifts in the upper part of the Galena limestone above the flint beds. The main drift is 6 to 8 feet wide and opened into a large cave 12 feet wide, the bottom of which was filled with loose rock and ore. A crevice extended upward from the cave and the walls of the cave were coated with sulphides. This deposit lies below the Maquoketa shale and above the flint beds and almost the entire thickness of Maquoketa shale remains at the east end of the crevice.[31]

In Iowa nearly all the ore mined has come from the Dubuque district, although some galena has been mined from the districts northwest of Dubuque near the Mississippi river. The Dubuque mines were among the first in the United States to be developed and at one time they were the most productive lead mines in the United States. The country is an area of gently folded Ordovician beds including the Galena limestone and the Maquoketa shale. The axes of the folds strike east and closely spaced fissures or crevices also strike east. The crevices are followed from 1 to 2 miles on strike. All the mines are in the Galena dolomite and practically all the ore has come from the horizon above the cherty part of the Galena in the upper 100 feet of the formation. By far the largest amount of the ore has come from the upper part of the formation that lies within 50 feet of the base of the Maquoketa shale. The crevices are verticals, and flats and pitches are practically wanting. The ore shoots are horizontal bodies or runs which are developed where the crevices cross favorable beds. The upper run or opening which is most productive is 40 feet below the shale in a heavy bedded dolomite below thin bedded dolomite. The first opening is usually 4 feet high, but at places chimneys extend up to the shale. The second openings are also in heavy bedded dolomite and are found 45 feet below the first. The third openings are about 26 feet below the second openings and near the top of the flint beds. A fourth opening is found locally in the top of the flint beds.

The lead-zinc district of the upper Mississippi valley extends northwest into southeastern Minnesota. Over a wide area pseu-

[31] *Idem*, p. 58.

domorphs of marcasite are found in limestone and in the village of Dresbach galena ore was once mined. It occurs in a bed of shale in the St. Croix sandstone of Cambrian age. The deposit is in a crevice 4 feet wide at the surface which narrows in depth. The crevice or vein occupies a fault fissure.[32] The ore is made up of galena and pyrite and is found in the fissure and disseminated in the country rock on either side of the fissure. Some of it in the fissure is a cemented breccia.

Although the amount of throw of the fault can not be made out the geologic sections on either side of the fault published by Winchell show that the throw is considerable. Galena and cerussite occur in veinlets in limestone above the mine.

SUMMARY.

The supporters of the theory that the deposits of sulphide ores of the Mississippi Valley were formed by precipitation from meteoric solutions moving downward or laterally have based their conclusions on the belief that the rocks below the deposits include shales that would halt upward-moving waters and that fracturing and faulting are not sufficient to break the rocks so as to provide upward channels. The supporters of the theory that the ores were deposited by rising meteoric waters recognize the impervious character of certain shales, but believe that openings are provided along faults and also where the shales were locally partially removed by erosion at unconformities before the rocks containing the ores were deposited. A heavier burden lies upon the supporters of the theory that the deposits were formed by rising thermal waters, for such waters have probably come from great depths.

In the regions containing the deposits there is as a general rule very little shale in the Paleozoic beds below the rocks containing the ores. What is below the Paleozoic beds is not known. In most of the regions containing the ores faulting is recognized and the recent work done by various surveys shows that faulting is very common along the major zone of deformation of the

[32] Winchell, N. H., Geol. of Minn., vol. 1, p. 258, 1884.

Mississippi valley along which all the ores are found except the lead and zinc ores of the upper Mississippi valley in Wisconsin and Illinois. In the disseminated lead district of Missouri no continuous shale beds are found below the Davis shale and the chief deposits are below the Davis shale. In the barite district of Washington County the ores are in rocks that lie above the Davis shale. This shale is 169 feet thick in the lead district but its thickness below the barite ores is not known. There are, however, great faults in the barite district and steep, banded veins, one of which has been worked to a depth of 480 feet. In the lead and zinc district of Central Missouri the ores are found chiefly in Cambro-Ordovician rocks. Below some of the deposits the St. Elizabeth formation probably contains shales.

In the Joplin region thin shales are probably present at places below the ore deposits. The region is in the strike of the Seneca fault zone which contains faults with vertical displacements of several hundred feet. These faults are not followed into the main ore bearing district although faults with small throw, some of them parallel to the faults of the Seneca group, are recognized at several places.

In northern Arkansas shales are found below the zinc deposits that lie in the Boone formation. The chief deposits, however, are in the Yellville limestone of the Ordovician. This region contains faults that are followed 7 miles on strike and that have considerable displacement. In the Batesville manganese district no shales are known in the rocks exposed that lie below the deposits. Faults are present in the area and the largest mine is near a fault that is followed several miles and has a displacement of 400 feet. In southern Illinois and western Kentucky the fluorspar deposits are in great fault fissures. In southwestern Wisconsin zinc district there is no thick shaly series below the main ore bodies except in the Cambrian sandstones. These sandstones are exposed along the Wisconsin river and contain shale layers there but the shales are lenses rather than continuous bodies.

In the three most important ore-bearing areas of the Mississippi valley, as shown by Fig. 14, the ore is in the highest limestone

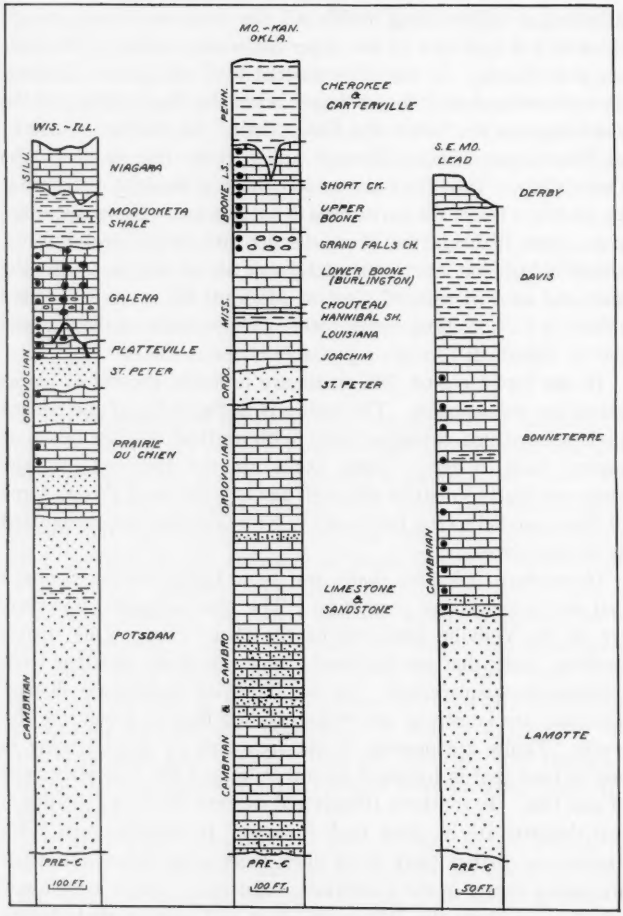

FIG. 14. Generalized geologic sections of the main ore-bearing areas of the Mississippi valley. The chief horizons of the ore deposits are marked by dots and in each district the chief deposits are in the highest limestone series, below the lowest thick shale series of the district.

series that lies below the lowest thick shale series. In Wisconsin the ore is below the Maquoketa shale and no important deposits are above the base of the Maquoketa shale. In the Flat River district the disseminated lead ore is below the Davis shale. In the Joplin region the ore is below the Coal Measures shale and in the Batesville region, Arkansas, it is in and below the Cason shale.

In the barite district of Missouri, however, the barite deposits are above the Davis shale, but great faults pass through the area. In the disseminated lead ore district, Missouri, and in the Batesville manganese ore district, Arkansas, a considerable number of the largest deposits are in anticlines below shales.

Vertical zones are recognized at a few places. In northeast Oklahoma, in the primary ore, lead predominates at higher elevations and zinc at lower ones. The same is probably true in the Wisconsin district although secondary alteration has greatly emphasized this zoning. The Rosiclare mine in the fluorite bearing district of southern Illinois is 725 feet deep and is, I believe, the deepest mine in the Mississippi valley region that yields sulphide ores. At depths above 200 feet below the surface lead predominates and below that depth zinc increases and lead is practically wanting.

Horizontal zones are well shown in the Ozark region. A disc of iron sulphide ores with specularite and rose quartz is surrounded by a belt of iron sulphide ores without specularite and the latter is surrounded by a belt of ores of lead, zinc, and barite. South of the latter the manganese ores of Batesville, Arkansas, appear. These ores and the fluorite ores of southern Illinois and eastern Kentucky may belong to a fourth zone but that is uncertain.

In Wisconsin a belt including gold with rose quartz, copper ores, and zinc and lead ores, strikes northwest and zinc and lead ores with little or no copper are found on either side of it. This zoning, although imperfect, is noteworthy. Since the zones are in the same order as that shown in zoned areas of ore deposits closely associated with igneous rocks, it appears probable that the

sulphide ores of the Mississippi valley are also associated with igneous rocks.

All the sulphide ores of the Mississippi valley except the silver tungsten ores of the Einstein mine are believed to be of the same age. All the ores are in Paleozoic or older rocks and they were probably formed at about the time of the Appalachian revolution since some of them are in strata of the Coal Measures. The chief ore deposits of the southern Appalachian Mountains and of the Ouchita Mountains are probably of the same age. The reasons for this conclusion are as follows: if the deposits are platted on a geologic map it is found that all lie in Paleozoic or older rocks. In certain regions the deposits are closely spaced near the edges of the Paleozoic area. Although post-Paleozoic rocks border the metallized areas for many miles, no ores are found in them in the Mississippi valley except sedimentary iron ores and aluminum ores.

In Pike County, Arkansas, a few peridotite intrusives cut the Trinity (Lower Cretaceous). Some of them contain diamonds. It is believed that they are later than the metalliferous ores and that the peridotites are later than the intrusives that lie in Paleozoic rocks in Arkansas, Oklahoma, Missouri, Kansas, Kentucky and Illinois. The intrusives in the Lower Cretaceous and the associated diamond deposits mark a later period of igneous activity in the Ouchita-Ozark region just as the Triassic intrusives with associated ores of iron and other metals mark a later period in the Appalachian region.

The Appalachian Mountains and the Ouchita-Arbuckle-Wichita Mountains were formed at about the same time. Branner groups them in a single mountain system. Many have objected to this grouping yet there is some structural evidence that supports it, for the major zone of deformation of the Mississippi valley may be regarded as a foothill system of faults and folds that has the same relations to both mountain systems. This is shown by Figure 1, which shows the Chestnut Ridge-Warfield-Campton-Rough Creek-Bald Hill-Ozark-Seneca zone and its relation to the Appalachian and Ouchita groups. These two groups of

mountains and the major zone of deformation of the Mississippi valley were formed at about the same time. This structural evidence is strongly supported by the grouping of the metalliferous sulphide deposits which, with the exception of Triassic deposits in the Appalachian region, are confined to the Paleozoic and older rocks.

In the Appalachian region the chief deposits are related to the granitic rocks that were intruded near the close of the Paleozoic era. This is shown by their locations with respect to such rocks and to each other, since most of them are zoned and the zones lie in normal order. In the Ouchita region of Arkansas and Oklahoma there are many intrusives and small metalliferous deposits are closely spaced. There is little evidence of zoning yet the positions of the deposits with respect to the intrusives suggest a generic relation.

In the belt of deposits extending from eastern Kentucky to Oklahoma intrusives are not closely spaced, yet they are found at many places. Basic dikes occur in eastern Kentucky, in western Kentucky and southern Illinois, near Avon, Ste. Genevieve County, Missouri. A granite pegmatite is found in Camden County, Missouri, and a granite at Spavinaw, northeastern Oklahoma, and igneous rocks occur in southeastern Kansas. All these intrusives are in Paleozoic rocks and all of them are probably of late Paleozoic age, except the Spavinaw granite, which is older, and possibly the Camden County pegmatite. The intrusives, with the two exceptions named, may be of the same age as the granite of the southern Appalachians which Keith has shown to be of late Paleozoic age. These structural relations and the relations of the ore deposits, to structure and to each other, support the hypothesis that the ores have been deposited by thermal waters rising from a deep seated igneous mass of which the basic and acid rocks of the region are upward extensions.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS.

SOLUTION, TRANSPORTATION AND PRECIPITATION OF IRON AND SILICA.[1]

E. S. MOORE AND J. E. MAYNARD.

PART I.

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INTRODUCTION.

THIS problem has been studied for decades by chemists and geologists but many of its phases remain unsolved. There are also many conflicting opinions regarding the results of experimental work and their place in geological processes. The puzzling problem of the genesis of the extensive iron formations, particularly the siliceous, banded types of the pre-Cambrian group, remains unsettled. It is admitted by all investigators that tremendous quantities of iron and silica are carried in solution by the streams of the world but no deposits exactly similar to those formed in pre-Cambrian time are being formed to-day. Also, in the Palaeozoic and later limestones, large quantities of chert have been formed either through replacement or by direct precipitation of silica in sea water.

The importance, therefore, of a further study of the behavior of iron and silica in solution led the writers to undertake an investigation of this problem with the hope that some of the conflicting statements bearing on it might be reconciled and that

[1] Published by permission of the National Research Council of Canada.

fresh data might be secured from experimental work. The results so far obtained seem to have cleared up a number of controversial points and to have extended considerably our knowledge of the behavior of these elements in solution under natural conditions. There is so much detail in a paper of this sort that the writers have thought it best to make frequent summaries of results and conclusions even to the extent of running the risk of criticism for duplication. It is hoped that this will make it possible for the reader more easily to keep in mind the details of each phase of the experimental work.

The laboratory work connected with this investigation was performed by the junior author, while the senior author is chiefly responsible for the opinions expressed regarding the origin of the iron formations.

ACKNOWLEDGMENTS.

The writers acknowledge their indebtedness to the National Research Council of Canada for a grant which made this investigation possible. They are particularly indebted to Professor J. W. Bain of the Department of Chemical Engineering and to Professor L. J. Rogers of the Department of Chemistry in the University of Toronto for advice on chemical matters and for the use of apparatus. Mr. D. R. Derry performed some laboratory work on the origin of iron carbonate deposits for which thanks are due. For collecting and forwarding samples of water and rocks the writers express their appreciation to Mr. M. J. Skillen of Fort William, and Mr. G. B. Tribble of Creighton Mine, Ontario, and Mr. A. R. Lanigan, Calumet, Quebec.

GENERAL SUMMARY.

This research, of necessity, involved a great amount of chemical work in order to determine, if possible; (1) the amount of iron and silica in natural waters, (2) the agents by which these substances were taken into solution, (3) the final chemical state of the iron and silica in the solution permitting transportion, and, (4) the manner of precipitation of the silica and iron to form the characteristically banded precipitates, and the agents which brought about this precipitation.

Quantity of Iron and Silica in Natural Waters.

Tarr,[2] using Clark's data, calculated that 222,200,000 tons of silica is being carried annually to the sea by the rivers of the world. The quantity of silica is exceeded by that of only one base, calcium. Thus, at the present day most of the large rivers of the world are transporting sufficient silica to form a large sedimentary iron formation, but such a statement cannot be made for iron. There are some rivers, however, transporting considerable quantities of iron.

The Amazon river at Obides carries from 3.6 to 6.2 parts per million $Al_2O_3 + Fe_2O_3$, 9.4 to 12.2 parts per million SiO_2, and 5.7 to 8.9 parts per million organic matter. Gruner[3] has calculated that the Amazon, assuming the iron content to be 3 parts per million, could carry sufficient iron in 176,000 years to form the Biwabik formation. Thus, large rivers, rich in organic matter, could transport, during a great number of years, sufficient iron to form a large sedimentary iron deposit. The amount of silica transported would be correspondingly large.

There are a great many rivers, other than the Amazon, transporting more than 3 parts per million iron, and 9 parts per million silica, among which are the streams of British Guiana and Argentine of South America, and the Indalself river of Sweden.[4]

In North America the average iron content of river waters is less than one part in a million, but there are streams and lakes in which it is considerably higher. Among these are waters from the Lac-a-la-Tortue district, Quebec, and the English river district, Ontario, Samples of these waters were analyzed and the following results and conclusions were arrived at:

1. Samples of water from Lac-a-la-Tortue, Quebec, taken from two different points, gave on analysis 1.8 and 2.5 parts per million ferric oxide. A sample from the outlet of the lake gave 2.8 parts per million ferric oxide, one from the most easterly of two creeks entering the lake, 5.2 parts ferric oxide, and one from

[2] Tarr, W. A., *Amer. Jour. Sci.*, 44, p. 430, 1917.

[3] Gruner, J. W., ECON. GEOL., 17, p. 454, 1922.

[4] Clark, F. W., Data of Geochemistry, U. S. Geol. Surv. Bull. 770, pp. 74–119, 1924.

the creek flowing into the south end of the lake, 6.6 parts ferric oxide.

2. Samples of water from Calumet lake, Quebec, gave 1.3 parts per million ferric oxide and samples from the creek flowing into the north end of the lake showed 2.2 parts per million of this oxide. Those from the creek flowing out of the south end of Calumet lake contained 1.8 parts per million ferric oxide.

3. Samples of water from Hematite lake, near Niblock, in the English river area, Ontario, gave on analysis 3.8 parts per million, those from Beaver creek, 14.4 parts per million and those from Fox creek, 8.6 parts per million ferric oxide.

4. Smaller quantities of iron are now being transported and deposited in the bog lakes of Quebec than must have been transported and deposited to form the bog ores mined in the past.

5. Organic matter plays an important role in the solution and transportation of bog lake ores. The proportion of iron carried depends upon the quantity of organic matter in solution.

6. The quantity of silica in these waters constitutes a relatively small percentage of their total mineral content.

7. The proportions of lime, magnesia, and bicarbonate radicle do not materially affect the proportions of iron carried in these natural waters.

Solution of Iron and Silica.

The work of numerous investigators has established the fact that reagents such as carbonated water, oxygenated water, solutions of magnesium and calcium bicarbonate, acids and alkalies, and peat solutions are effective solvents of silica from rocks and minerals. Less work has been done on the solution of iron, but it is known that carbonated water, solutions of organic matter, and these in combination with various salts, are effective solvents of iron from rock-forming minerals containing iron.

In this connection a series of experiments was carried out to determine the relative amounts of iron and silica dissolved from norite and diabase by distilled water, oxygenated water, carbonated water and solutions of organic matter. The effect on the quantity of iron and silica dissolved from the rocks upon

increasing the time of their contact with the various solutions was studied. The effect on the quantity of iron and silica dissolved upon grinding the rocks to different degrees of fineness was also determined.

The results in condensed form are given below:

1. Carbonated water is the most effective solvent of iron and silica from norite and diabase.

2. Peat solution is the next most effective solvent of iron and silica.

3. Distilled water is a very poor solvent of iron, but it is a fairly active solvent of silica.

4. Oxygenated water is a very poor solvent of iron and only a fair solvent of silica.

5. In general, fine grinding increases the solvent action of the various reagents, 48-mesh norite in 70 days yielding more iron and silica than 10-mesh norite, and 150-mesh diabase in 70 days yielding more iron and silica than 48-mesh.

6. Time is an important factor in the solution of iron and silica from norite and diabase by distilled water, oxygenated water, and carbonated water, for invariably more iron and silica are dissolved by these reagents in 287 days than in 70 days. Carbonated water in 287 days dissolved 45.8 parts per million ferric oxide, 89.2 parts per million silica from norite, and 11.8 parts per million ferric oxide and 50.0 parts per million silica from diabase. Peat solutions in 287 days dissolved 7.6 parts per million ferric oxide and 52 parts per million silica from norite, also 12.8 parts per million ferric oxide and 47.2 parts per million silica from diabase.

7. The general conclusion is that carbonated water is able to dissolve sufficient iron and silica from a basic terraine to form a large sedimentary iron deposit. Organic matter, if present, assists also in dissolving much iron and silica. Inorganic acids, under exceptional circumstances, cause much iron and silica to go into solution.

Transportation of Iron and Silica.

Formerly it was believed that most of the iron was transported by surface waters as sulphate, chloride, bicarbonate, and salts of organic acids, the greater portion being in the form of bicarbonate. More recently it has been advocated that iron is transported as a colloid or that it is adsorbed by organic colloids. Similarly it was first thought that silica was transported as silicates of the alkalies, but it is now generally accepted that the greater portion is carried as a colloid.

The above conclusions, especially those relating to iron, were based on theory rather than on experimental evidence, whereas the following results are based on actual experiments, a description of which is given in the main text:

1. Iron is not carried as bicarbonate in cold, natural surface waters high in organic matter, but in all probability it is transported as a ferric oxide hydrosol stabilized by organic colloids. A relatively small amount may be carried as salts of organic acids or adsorbed by organic colloids.

2. As much as 36 parts per million ferric oxide, formed by the oxidation and hydrolysis of ferrous bicarbonate can be held in colloidal solution by 16 parts per million organic matter.

3. Under exceptional conditions iron may be in solution in surface waters as salts of inorganic acids or as a ferrous silicate hydrosol.

4. Silica in solution in cold, natural waters is transported as a colloid provided the concentration does not exceed 25 parts per million but if the concentration is higher it is possible for a small percentage to be transported as alkaline silicate.

5. The general conclusions are: (1) that the iron going to make up some of the large sedimentary iron formations was transported principally as a ferric oxide hydrosol, stabilized by organic matter, and (2) that the greater portion of the silica was transported as a silica hydrosol.

Precipitation of Iron

Precipitation of Ferric Oxide Hydrosols by Electrolytes.—Ferric oxide hydrosols were formed: (1) by hydrolyzing a solu-

tion of ferric chloride, (2) by dispersing freshly precipitated ferric hydroxide in a solution of ferric chloride, and (3) by oxidizing a solution of ferrous bicarbonate in the presence of a small amount of peat solution. The ferrous bicarbonate solution was obtained by the action of carbonated water on norite.

Individual electrolytes, in proportions similar to their concentration in sea water, that is 34,400 parts per million, were added to ferric oxide hydrosols made by the first two methods mentioned above and containing 10 parts per million ferric oxide. Sea salt in the proportion of 34,400 parts per million was added to a ferric oxide hydrosol made by the third method and containing 36 parts per million ferric oxide. The following results were obtained:

1. Sodium chloride, potassium sulphate, magnesium sulphate, potassium chloride, potassium nitrate, and sodium hydroxide each cause, almost immediately, complete precipitation of the first two types of ferric oxide hydrosols.

2. Sea salt (that is, salt obtained from the evaporation of sea water) in the proportion of 34,400 parts per million, also caused, almost immediately, complete precipitation of the first two types of ferric oxide hydrosols.

3. Sea salt, in the proportion of 34,400 parts per million, does not cause immediate precipitation of the third type of ferric oxide hydrosol, but at the end of three days complete coagulation takes place.

Precipitation of Iron from Solutions of Organic Salts of Iron by Bacteria.—A series of experiments was performed on the precipitation of iron from solutions of organic salts of iron by bacteria such as exist in muck, soil, and natural waters. Experiments were also made to determine whether the rate of precipitation would be affected by exclusion of light, by oxygen, or by carbon dioxide. The experiments consisted of inoculating the solutions with muck, soil, or natural water and then exposing them to light, or keeping them in darkness, or impregnating them with oxygen or carbon dioxide. The results are as follows:

1. Iron is precipitated by bacteria as ferric hydroxide from

solutions of ferric ammonium tartrate, ferric malate, ferric formate, and ferric tartrate.

2. Light has no appreciable effect on the rate of precipitation of ferric hydroxide by bacteria.

3. Carbon dioxide or oxygen do not materially affect the precipitation of iron by bacteria.

4. The organisms in the natural waters of Calumet lake, Quebec, and Hematite lake, Ontario, are able to precipitate iron in the laboratory as ferric hydroxide from ferric ammonium tartrate solutions.

5. These soil bacteria, capable of precipitating organic iron solutions, are very widespread in nature.

Precipitation of Silica

Precipitation of Sodium Silicate Solutions.—(*a*) Precipitation by electrolytes: The precipitating effect of individual electrolytes and the combined effect of sea water electrolytes were determined for sodium silicate solutions of various concentrations. The results are as follows:

1. Electrolytes such as sodium chloride, potassium sulphate, carbon dioxide, or calcium bicarbonate do not immediately precipitate silica from dilute sodium silicate solutions. Sodium chloride, potassium sulphate, and calcium bicarbonate, however, with time do precipitate the silica.

2. Sea water does not immediately precipitate silica from dilute sodium silicate solutions, but with time it does act as a precipitant.

3. Sea water and calcium bicarbonate are the most efficient precipitants of silica from dilute sodium silicate solutions. Potassium sulphate and sodium chloride are not as effective.

4. Magnesium sulphate, with solutions of sodium silicate containing less than 25 parts per million silica, gives no precipitate, but if the concentration of sodium silicate is increased a precipitate immediately forms. This precipitate, however, does not appear to be gelatinous silica, and this has been found to be magnesium silicate with excess silica.

5. Carbon dioxide and magnesium sulphate act as stabilizers in solutions of sodium silicate containing less than 25 parts per million silica.

(*b*) Precipitation by magnesium sulphate: As mentioned in the previous section magnesium sulphate gives practically no precipitate with sodium silicate solutions containing 30 parts per million silica, whereas with sodium silicate solutions of greater concentration magnesium sulphate gives, immediately, a heavy white precipitate. It was thought that this precipitate might be magnesium silicate and that our conception of the dilution at which sodium silicate is completely hydrolyzed will have to be changed. With this point in view a series of experiments was performed.

Sodium silicate solutions of various concentrations were prepared and magnesium sulphate in excess was added to each, with the following results:

1. Magnesium sulphate causes an immediate precipitation in all sodium silicate solutions containing more than 25 parts per million silica, but in no case with concentrations up to 480 parts per million does complete precipitation of the silica take place.

2. The precipitate is a silicate of magnesium of the composition $MgO.2.3.4.5SiO_2$, not gelatinous silica, and it probably consists of $MgO.SiO_2$ and excess silica.

3. Magnesium sulphate reacts by double decomposition with silica in solution as sodium silicate, forming the magnesium silicate, but it does not react with silica in colloidal solution.

4. The less the concentration of a sodium silicate solution, the greater is the proportion of the silicate hydrolyzed and consequently the smaller is the amount of magnesium silicate precipitated by magnesium sulphate.

5. The general conclusion from these results and those of Bogue is that at a dilution of 25 parts per million silica, sodium silicate solutions are completely hydrolyzed, the silica all being in the colloidal form. This result is very much lower than that obtained by Kahlenberg and Lincoln, who state that sodium silicate solutions are completely hydrolyzed at a dilution of 1257 parts per million silica.

Precipitation of Silica Hydrosols.—(*a*) Precipitation of silica hydrosols formed by dialyzing a solution of sodium silicate.

Precipitation by electrolytes: Sodium silicate solutions were dialyzed until free from ions, diluted to the required strength and the chosen electrolyte added. A summary of the results follows:

1. Sodium chloride of the concentration of sea water, that is, 34,400 parts per million, or sea water itself, are among the most efficient precipitants of the silica hydrosol.

2. Saturated solutions of magnesium or calcium bicarbonate are very inefficient precipitants of the silica hydrosol.

3. Magnesium sulphate, of the concentration of sea water, is a very inefficient precipitant of the silica hydrosol. During the time of experimentation (75 days) it tended rather to act as a stabilizer of the silica hydrosol.

4. In no case, during the time of experimentation, did complete precipitation of the silica hydrosol by electrolytes take place.

5. Time is the outstanding factor in the precipitation of this type of silica hydrosol by electrolytes.

(b) Precipitation of silica hydrosols formed by dialyzing a mixture of sodium silicate and hydrochloric acid.

Precipitation by electrolytes: A mixture of measured proportions of sodium silicate and hydrochloric acid was dialyzed until free from ions, diluted to the required strength, and the chosen electrolytes added. A resumé of the results follows:

1. Sea water, with time, is an efficient precipitant of the silica hydrosol.

2. Sodium chloride of the concentration of sea water up to the end of 75 days showed no precipitating effect on the silica hydrosol.

3. Saturated magnesium bicarbonate, and calcium bicarbonate are very inefficient precipitants of the silica hydrosol.

4. Magnesium sulphate of the concentration of sea water during the time of experimentation (75 days) acted as a distinct stabilizer of the silica hydrosol.

5. Time is the important factor in the coagulation of this type of silica hydrosol by electrolytes.

6. In no case during the time of experimentation did complete coagulation of the silica hydrosol take place.

Precipitation by calcium or magnesium bicarbonate: Silica hydrosols of various concentrations (formed by dialyzing a mixture of sodium silicate and hydrochloric acid) were treated with magnesium carbonate and carbon dioxide, and calcium carbonate and carbon dioxide.

1. Magnesium bicarbonate or calcium bicarbonate, even allowing long periods of time, are inefficient precipitants of this type of silica hydrosol containing 30 parts per million silica.

2. Magnesium bicarbonate or calcium bicarbonate do not immediately precipitate silica hydrosols containing from 60 to 100 parts per million silica. These electrolytes, however, with time, do precipitate part of the colloidal silica.

3. Magnesium bicarbonate and calcium bicarbonate coagulate, almost immediately, silica hydrosols of very high concentrations. Inert substances such as carbon dioxide and calcium carbonate, also coagulate silica hydrosols of very high concentrations.

4. Concentration and time are two important factors in the precipitation of silica hydrosols of this type by magnesium and calcium bicarbonate.

5. Silica hydrosols of this type and of such concentrations as exist in natural waters are rarely coagulated by calcium or magnesium bicarbonate.

Effect of concentration and time: The effect of concentration and time on the precipitation, by sea electrolytes, of silica hydrosols containing varying proportions of silica (formed by dialyzing a known mixture of sodium silicate and hydrochloric acid) was determined:

1. Sea salt, up to the concentration of the ocean almost immediately coagulates a silica hydrosol of this type containing 30,000 parts per million silica, whereas at a concentration of 25 parts per million silica coagulation is not complete in six months.

2. The general conclusion reached is that the lower the concentration of a silica hydrosol the greater is the time required for its coagulation by electrolytes of the sea.

General Discussion of the Precipitation of Silica.—A brief statement of the results obtained by various investigators of the precipitation of silica, and the manner in which they differ from those of the writers, follows:

Tarr determined that artificial sea water, or sodium chloride, or magnesium sulphate, would immediately coagulate silica from sodium silicate solutions that were so diluted that they contained 27.07 parts per million silica. The writers, repeating these experiments, obtained entirely different results. In no case did the silica coagulate immediately on adding the electrolytes, but with time, artificial sea water, and pure sodium chloride did bring about precipitation of the silica. On the other hand magnesium sulphate acted more as a stabilizer than a precipitant of the silica. Results similar to those of Tarr, were obtained on reproducing the magnesium sulphate experiments with sodium silicate solutions containing 300 parts per million instead of 27.07 parts per million silica. The precipitate, however, was found to be magnesium silicate with excess silica. This result was due to the fact that at a concentration of 300 parts per million silica the solutions were only partially hydrolyzed, the greater portion of the silica being still in solution as sodium silicate, thus permitting reaction with magnesium sulphate to form insoluble magnesium silicate. Magnesium sulphate does not react with colloidal silica. From these results it would appear that Tarr used sodium silicate solutions of far higher concentrations than he was aware.

Dean found that colloidal silica solutions, formed by dialyzing a mixture of water glass and hydrochloric acid, were precipitated within an hour by calcium bicarbonate. Lovering, experimenting with the same type of colloidal solution, found that precipitation did not take place in dilute solutions, but that if the concentration was over 40,000 parts per million, precipitation occurred. From this result he concluded that calcium and magnesium bicarbonate solutions were solvents of silica in nature. The writers, repeating the experiment, were unable to obtain an immediate precipitate with dilute colloidal silica solutions, but they did obtain a precipitate with those which were concentrated. After two

months, however, partial precipitation had occurred in the dilute solutions, although at dilutions as low as 30 parts per million the greater portion of the silica remained stable. These results are more in accord with those of Lovering and it is probable that calcium and magnesium bicarbonate at such concentrations as exist in nature rarely act as precipitants of this type of colloidal silica.

Conclusions reached regarding the formation and precipitation of colloidal silica are:

A variety of types of colloidal silica can exist in nature. With time all these types can be precipitated by electrolytes of the sea. The rate of precipitation depends upon the concentration of the silica hydrosol. The type of colloidal silica determines the electrolyte that will act as the most efficient precipitant.

Mutual Precipitation of Ferric Oxide and Silica Hydrosols.

Experiments on mixing ferric oxide and silica hydrosols showed that:

1. Ferric oxide and silica hydrosols taken separately are quite stable, but when they are mixed mutual precipitation occurs.

2. On mixing colloidal silica and colloidal ferric oxide in such proportions that the total reaction mixture contains 30 parts per million silica and 10 parts per million ferric oxide, practically all the iron, together with a little silica, is precipitated, whereas the greater portion of the silica remains stable.

Stabilization of Ferric Oxide and Silica Hydrosols.

As mentioned in the previous section, ferric oxide and silica hydrosols when mixed mutually precipitate each other. Also ferric oxide hydrosols dialyzed in tap water are relatively unstable, coagulation taking place in a few weeks. In an effort to prevent precipitation of these compounds a series of experiments was performed, and the results obtained are summarized below:

1. Colloidal ferric oxide, dialyzed in tap water, remains stable for at least six months, providing a small amount of peat solution is present.

2. A colloidal solution, containing 30 parts per million silica

and 10 parts per million ferric oxide, remains stable, providing 9 parts per million organic matter is present.

Precipitation by Electrolytes of Ferric Oxide and Silica Hydrosols Stabilized by Organic Matter.

The precipitating effect of sea electrolytes on stable colloidal solutions containing iron and silica was determined. These solutions can be formed (1) by mixing ferric oxide and silica hydrosols in the presence of a small quantity of peat solution, (2) by oxidizing a solution of ferrous bicarbonate, obtained by the action of carbonated water on norite, in the presence of a small quantity of organic matter. A summary of the results follows:

1. Sea salt, in the proportion of 34,400 parts per million, precipitates in 12 hours the greater portion of the iron from a colloidal solution formed by the first method and containing 30 parts per million silica, 10 parts per million ferric oxide and 9 parts per million organic matter. The greater portion of the silica is not precipitated, however, until after four months.

2. Sea salt, in the proportion of 34,400 parts per million, precipitates in three days the greater portion of the iron from a colloidal solution formed by the second method and containing 73.8 parts per million silica, 36 parts per million ferric oxide, and 16 parts per million organic matter, whereas the greater portion of the silica is not precipitated until after seven months.

3. The conclusion is that ferric hydroxide is precipitated in a few days when colloidal iron and silica solutions, stabilized by organic matter, come in contact with electrolytes of the sea, whereas silica is not completely coagulated after several months.

Banding of Iron and Silica.

The banded pre-Cambrian iron formations are well known, but very few suggestions have been made regarding the cause of the banding. With the object of throwing more light on this problem a number of experiments were performed.

Banded iron and silica can be produced in the laboratory by Liesegang's method, that is, by the diffusion of a soluble hydrox-

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Banded iron and silica can be produced in the laboratory by Liesegang's method, that is, by the diffusion of a soluble hydrox-

ide into a silica gel that has previously been impregnated with a soluble iron salt. This method, however, does not seem adequate to explain the large banded iron formations.

Banded iron and silica can also be produced by the differential settling in sea water of freshly precipitated and well agitated ferric hydroxide and silica. The greater portion of the iron with considerable silica settles first, followed by the deposition of a layer of almost pure silica. New supplies of the material will cause a repetition of the banding.

In the preceding section it was shown that ferric hydroxide is precipitated in a few days when colloidal solutions, containing iron and silica stabilized by organic matter, are subjected to the influence of electrolytes of the kind and concentration found in the sea, whereas the silica is not coagulated after several months This result suggested that if a fresh supply of material were added the process would be repeated, giving a banded structure, and such was found to be the case.

QUANTITY OF IRON IN NATURAL WATERS.

Clark [5] calculated that the average iron content of the river and lake waters of North America is less than one part in one million, and that for the world it is less than 2 parts in one million. There are rivers, however, that carry a fairly high content of iron. The river waters of British Guiana carry up to 7 parts per million Fe_2O_3.[6] They are brown in color, low in salinity, and rich in organic matter. The color is supposed to be due to organic compounds of iron. The waters from the Amazon river and its tributaries carry from 2 to 7 parts per million Fe_2O_3.[7] Organic matter [8] constitutes 15.03 per cent of the dissolved solids of the Amazon.

Swamp waters in general appear to be higher in iron than other waters. Moore [9] found that samples of water collected

[5] Clark, F. W., *op. cit.*, p. 119.
[6] *Idem*, p. 94.
[7] *Idem*, p. 96.
[8] *Idem*, p. 96.
[9] Moore, E. S., Econ. Geol., 5, p. 533, 1910. 18th Rept. Ont. Bur. of Mines, p. 192, 1909.

from the most easterly of the Little Bear lakes, Thunder Bay district, Ontario, and from the main creek entering the lake, contained respectively 56 and 61 parts per million Fe_2O_3. Analyses also were made of the waters in the vicinity of Hematite lake, Niblock, Ontario. The sample taken from near the head waters of the creek flowing into Hematite lake contained 47 parts of Fe_2O_3 while the sample collected from the same stream near the lake showed only 45 parts per million of Fe_2O_3. A sample collected from the stream draining Hematite lake gave 21 parts per million Fe_2O_3. Simpson [10] mentioned a stream that contained 17 parts per million of iron and much organic matter. Gruner [11] pointed out that the Amazon river, carrying an average of 3 parts of iron per million, in 176,000 years could transport 1,940,000 million metric tons of iron to the sea, which is the quantity assumed for the Biwabik formation. He also pointed out that the quantity of silica carried would be correspondingly large.

From the citations given above it is evident that the quantity of iron carried in natural solution depends to a great extent on the organic content of the streams.

Samples of water were collected from the Lac-a-la-Tortue district, Quebec, in November, 1926. The samples were analyzed in order to determine whether the streams were carrying and depositing, at the present day, the same quantity of iron that they had carried in the past. It is stated that Lac-a-la-Tortue has yielded paying quantities of bog ore from areas completely exhausted eight or ten years previously.[12] It has been said that the bog ores are renewed in the lakes of Sweden in twenty-five years.

The mineral analyses of the samples collected were made, in general, according to the method used by Dole,[13] the only variation being in the determination of iron and chlorine. The iron was determined by titration with potassium dichromate and the chlorine by the usual gravimetric method, that is, precipitation by

[10] Simpson, E. S., *Geol. Mag.*, 49, p. 405, 1912.
[11] Gruner, J. W., ECON. GEOL., 17, p. 455, 1922.
[12] Griffen, P. H., *Amer. Inst. Min. Eng.*, 21, p. 974, 1892–3.
[13] Dole, R. B., U. S. Geol. Surv., Water Supply Paper 236, 1909.

silver nitrate. The determination of the organic matter was made by a method given by Clowes and Coleman,[14] which consists essentially in determining the quantity of potassium permanganate required to oxidize the organic matter.

The results obtained by the analyses of the samples are given in Table I.

TABLE I.

ANALYSES OF WATER FROM THE LAC-A-LA-TORTUE DISTRICT, QUEBEC.

(Results in parts per million.)

	A.	*B.*	*C.*	*D.*	*E.*
Silica (SiO_2)	7.0	3.4	6.4	4.6	4.0
Iron Oxide (Fe_2O_3)	2.8	5.2	6.6	1.8	2.5
Calcium (Ca)	13.4	10.8	5.9	3.6	4.4
Magnesium (Mg)	1.6	1.8	1.5	1.1	1.2
Sodium (Na) / Potassium (K)	1.9	2.3	1.9	1.7	2.0
Carbonate (CO_3)	0.0	0.0	0.0	0.0	0.0
Bicarbonate (HCO_3)	39.0	29.3	20.1	9.7	14.6
Sulphate (SO_4)	11.2	16.0	9.8	8.7	7.6
Chloride (Cl)	0.4	Trace	Trace	Trace	Trace
Nitrate (NO_3)	.....	.....	.....	.....	.....
	77.3	68.8	52.2	31.2	36.3
Organic matter	8.6	14.0	18.4	8.8	7.8

A. From outlet of lake. Stream estimated at 12 feet in width with a depth of one foot. Current estimated at one mile per hour.

B. From most easterly of two creeks entering the lake on the southern side. Creek about 4 feet wide. Average depth one foot. Water somewhat brownish. Current sluggish, perhaps one-third of a mile per hour. Flows through sandy, grassy and somewhat shrubby area.

C. From second creek flowing into south end of lake on east side. Averages near lake about 3 feet wide and 6 inches deep. Water browner than from the other creeks. Current quite perceptible, perhaps one mile per hour. Flows over sandy and shrubby area.

D. From lake: Samples taken near the shore, in northwest corner of the lake, near the point where Mr. Bergeron said they used to dredge for iron. Shore sandy and marshy.

E. From lake: Sample taken along shore near point, on north side of lake, between point and west end of lake. Shore sandy and shrubby.

The analyses show that the two creeks flowing into Lac-a-la-Tortue are carrying 5.2 and 6.6 parts per million of Fe_2O_3 re-

[14] Clowes, F. and Coleman, J. B., "Quantitative Analysis," p. 301, 1914.

spectively, whereas the creek flowing out of the lake is carrying only 2.3 parts per million Fe_2O_3. This indicates that at least part of the iron has been deposited in the lake, as the two analyses of the lake water show only 1.8 and 2.5 parts per million Fe_2O_3. This variation in the iron content of the lake at the two different points is probably due to dilution by springs.

The quantity of iron being transported seems to depend on the organic matter in the streams. The amount of iron carried by the two creeks into the lake at the present time does not appear to be sufficient to form an economic deposit in ten years. Mr. J. A. Dresser [15] of Montreal thinks that this decrease in the quantity of iron being transported is due to a change in the general water level of the region. It is probable that much of the iron has entered the lake in water that has seeped out of the sandy area around the northwestern corner of the lake, rather than in water carried in the creeks.

TABLE II.

ANALYSES OF WATER FROM THE CALUMET DISTRICT, QUEBEC.

(Results in parts per million.)

	A.	*B.*	*C.*
Silica SiO_2	3.0	2.8	3.4
Iron Oxide (Fe_2O_3)	1.3	2.2	1.8
Calcium (Ca)	10.7	7.6	17.8
Magnesium (Mg)	1.6	1.8	1.4
Sodium (Na) / Potassium (K)	3.5	3.3	3.5
Carbonate (CO_3)	0.0	0.0	0.0
Bicarbonate (HCO_3)	31.7	8.6	36.6
Sulphate (SO_4)	14.0	18.5	17.5
Chloride (Cl)	0.8	0.6	3.2
Nitrate (NO_3)	....	....	....
	66.6	45.4	85.2
Organic Matter	5.7	12.8	6.4

A. Water obtained from Calumet lake, Quebec.

B. Water obtained from creek flowing into north end of Calumet lake.

C. Water obtained from creek flowing out of south end of Calumet lake.

An interesting feature is the rather high sulphate content. It is possible that a small portion of the iron is carried as sulphate.

[15] Personal communication.

Three samples of water[16] were obtained from the Calumet lake district, Quebec. A specimen of bog iron ore, obtained from the banks of the creek that flows out of the lake, was also forwarded.

The analytical results are given in Table II.

These data indicate that at the present time relatively little iron is being transported to Calumet lake. Whether this paucity of iron is due to the season when the samples were collected or to a lack of iron is not known. In order to determine this fact a series of analyses covering the greater portion of a year would have to be made. Relatively little silica is being transported. As in the case of Lac-a-la-Tortue, the quantity of sulphate is relatively large. Here, also, there is a marked relation between the organic matter and the iron content.

Samples of water (see Table III.) were obtained from the Hematite lake district, Niblock, Ontario.[17]

TABLE III.

ANALYSES OF WATER FROM THE NIBLOCK DISTRICT, ONTARIO.

(Results in parts per million.)

	A.	*B.*	*C.*
Silica (SiO_2)	9.8	5.6	7.4
Iron Oxide (Fe_2O_3)	3.8	14.4	8.6
Calcium (Ca)	6.4	7.4	3.6
Magnesium (Mg)	2.2	2.6	1.8
Sodium (Na) / Potassium (K)	3.3	4.2	2.4
Carbonate (CO_3)	0.0	0.0	0.0
Bicarbonate (HCO_3)	29.3	38.8	19.5
Sulphate (SO_4)	6.0	7.6	6.2
Chloride (Cl)	Trace	Trace	Trace
Nitrate (NO_3)	....	....	....
	60.8	80.6	49.5
Organic Matter	5.4	15.2	11.7

A. Water obtained from Hematite lake.

B. Water obtained from Beaver creek.

C. Water obtained from Fox creek.

[16] Collected October 29, 1926, by A. R. Lanigan of the International Magnesite Company, Limited, Calumet, Quebec.

[17] Through the kindness of Mr. M. J. Skilen, Fort William, Ontario.

The analyses show that more iron is being transported by the streams in the bog lake districts of Ontario than in those of Quebec. Beaver creek is transporting 14.4 parts per million iron oxide, while Fox creek is carrying 8.6 parts per million. The water from Hematite lake contains 3.8 parts per million iron oxide. These results are considerably lower than those obtained in 1908 by Moore,[18] for, as mentioned previously, the waters in the vicinity of Hematite lake, Niblock, Ontario, carried, at that time, from 21 to 47 parts per million Fe_2O_3. The probable explanation is that the iron content of these waters varies considerably with the seasons, the quantity of water in the streams, and the percentage of organic matter carried. Variations in the climate of each particular season may also play a part.

The analyses show, also, that the proportion of iron carried in solution is dependent upon the quantity of organic matter present in the water and that these waters are able to transport considerable quantities of iron.

Summary.—1. Very little iron is now being transported and deposited in the bog lakes of Quebec, such as Lac-a-la-Tortue, and Calumet Lake. It thus appears that owing to changes in water level or to the exhaustion of the iron supply in the sands through which the spring waters percolate, the bog lakes from which so much iron was obtained in the early days of the mining industry in Quebec are not depositing any appreciable quantity of iron.

2. Iron in considerable quantities is being transported and deposited in Hematite lake, Ontario, although the amount may vary considerably with the seasons, the climate of different seasons, the quantity of water in the streams, and the percentage of organic matter carried.

3. Organic matter plays an important rôle in the solution and transportation of bog lake ores; and the proportion of iron carried is dependent upon the relative quantity of organic matter in solution.

4. The proportions of lime, magnesia, and bicarbonate, do not

[18] Moore, E. S., Econ. Geol., 5, p. 533, 1910.

materially affect the proportions of iron carried. This fact indicates that the iron is either carried as salts of organic acids or as a ferric oxide hydrosol, stabilized by the organic colloids.

5. It is concluded that these results substantiate those of other investigators, that natural waters, rich in organic matter and of sufficient volume, can take into solution and transport, during a great number of years, sufficient iron to form a large sedimentary iron deposit.

QUANTITY OF SILICA IN NATURAL WATERS.

Clark [19] has compiled analyses of streams from all parts of the world. A few examples have been selected to illustrate the quantities of silica being transported at the present time. The Mississippi at New Orleans has an average silica content of 11.7 parts per million; the Nelson at its mouth, 13.0 parts per million; the St. Lawrence at Ogdensburg, 6.7 parts per million; the Amazon at Obides, 10.6 parts per million; and the Nile, below Cairo, 9.0 parts per million. A very conservative estimate of the silica content of the rivers of the world is 10 parts per million.

The silica content of the streams depends upon the terraine over which they flow. Invariably, the streams draining granitic and other igneous areas are higher in silica than those draining sedimentary and glacial areas.[20]

The number of tons of silica carried to the sea annually is enormous. United States Army engineers estimate that the flow of the St. Lawrence past Ogdensburg is 248,518 cubic feet per second. This volume of water with a salinity of 134 parts per million, transports annually [21] 29,722,000 metric tons of dissolved matter; of this amount 5.03 per cent. or 1,495,016 metric tons is silica. Tarr,[22] using Clark's data, calculates that 222,200,000 metric tons of silica is being added to the sea every year. Calcium is the only base that exceeds silica in quantity. Gruner [23]

[19] Clark, F. W., "Data of Geochemistry," U. S. Geol. Surv., Bull. 770, 1924.

[20] Tarr, W. A., *Amer. Jour. Sci.*, Ser. 4, 44, p. 429, 1917; Van Winkle, W., U. S. Geol. Surv. Water Supply Papers, Nos. 339 and 363; Clark, F. W., *op. cit.*

[21] Clark, F. W., *op. cit.*, p. 75.

[22] Tarr, W. A., *op. cit.*, p. 430.

[23] Gruner, J. W., ECON. GEOL., 17, p. 455, 1922.

calculates that the Amazon in 176,000 years can transport sufficient silica to form the Biwabik formation.

These citations are sufficient to show that large rivers, over long periods of time, can transport sufficient silica to the sea to form large sedimentary deposits. At the present time the greater portion of the silica entering the sea is being deposited with the clays and silts, but at times of peneplanation, when chemical denudation is at its maximum, the silica, as well as other chemical precipitates, might form almost pure deposits.

SOLUTION OF IRON AND SILICA.

The literature dealing with the solution of iron and silica is quite extensive and in most cases each substance has been studied separately.[24] Carbonated water was one of the first known solvents of iron, and the solubility of iron in carbonated water is due to the formation of the more soluble ferrous bicarbonate, which, however, has never been obtained in the solid state.

Gruner[25] found that carbonated water was an effective solvent of iron and silica from siderite, magnetite, olivine, and gabbro.

According to Leuhner and Merrill,[26] Calderon found that pure water dissolves silica to the extent of one part in 10,000, and that its solubility is increased by the presence of oxygen, carbon dioxide, nitric acid, small quantities of sulphuric acid, and especially humus acids.

Matignon and Mlle. Marchal[27] showed that silica can be dissolved in appreciable quantity by cold carbonated waters from hornblende, actinolite, epidote, chlorite, serpentine, "feldspar," adularia, oligoclase, olivine, wollastonite, muscovite, asbestos, talc, quartz, and dioptase.

[24] Rogers, W. E., and R. E., *Amer. Jour. Sci.*, *2*, 5, p. 401, 1848; Hauer, C. R., *Jour. Prakt. Chem.*, 81, p. 381, 1860; Wagner R., *Zeit. Anal. Chem.*, 6, p. 171, 1867; Delesse, A., *Bull. Soc. Geol.*, p. 311, 1873; Muller, R., *Tschermaks, Min. Mitteil*, p. 25, 1877; Henrich, F., *Zeit. Prakt. Geol.*, 18, pp. 85–94, 1910; Leitmuer, H., *Neues. Jahrb.*, Beil. Bd., 40 pp. 681–684, 1916; Smith, H. J., *Jour. Amer. Chem. Soc.*, 40, p. 879, 1918; Clark, F. W., U. S. Geol. Surv. Bull. 770, p. 535, 1924.

[25] Gruner, J. W., Econ. Geol., 17, p. 434, 1922.

[26] Leuhner, V. and Merrill, H. B., *Jour. Amer. Chem. Soc.*, 39, p. 2630, 1917.

[27] Matignon, M. C. and Mlle. Marchal, *Compt. Rend.*, 170, pp. 1184–1186, 1920.

Lovering [28] found that magnesium and calcium bicarbonate are very effective solvents of quartz, jasper, and taconite, and that sodium hydroxide is the most effective solvent of opal and chalcedony, and that it has, also, an appreciable effect on quartz, jasper, taconite, greenalite, actinolite and glauconite.

Clark [29] states that alkaline solutions have long been known to be solvents of silica in nature, and Dienert [30] attempts to give a logarithmic formula expressing the relation of alkalinity to the quantity of silica dissolved. Clark [31] further shows that when sulphates containing iron are oxidized, some iron is removed in solution as sulphate. Acids may be obtained by bringing solutions of neutral salts into contact with colloids or very porous substances.[32] The salts are broken up, the colloids or porous material adsorbing the base-forming element and liberating the acid. Gruner [33] gives this reason for salts such as sodium sulphate, sodium chloride, magnesium chloride, magnesium carbonate and calcium carbonate in the presence of peat, being so very effective in the solution of iron and silica from pyrite, magnetite, olivine, greenalite, and magnetic ferruginous chert, in the case of the sulphate and chloride solutions. The quantity of iron and silica taken into solution is very marked. Lovering [34] found that silicates, such as greenalite, actinolite, and glauconite are effectively acted on by dilute sulphuric acid and humic acid.

A brownish solution, colloidal in nature and possessing feebly acidic properties, may be extracted from decaying plants. This solution is reputed to be a powerful agent in the solution of rocks. Clark [35] believes that the disintegrating power is really due to carbonic acid resulting from the oxidation of the organic matter.

[28] Lovering, T. S., ECON. GEOL., 18, p. 528, 1923.

[29] Clark, F. W., U. S. Geol. Surv. Bull. 770, p. 478, 1924.

[30] Dienert, M. F., *Compt. Rend.*, 155, p. 797.

[31] Clark, F. W., *op. cit.*, p. 535.

[32] Cameron, F. K., and Bell, J. M., U. S. Dept. Agr., Bur. Soils Bull. 30, p. 39, 1905; Harris, J. E., *Jour. Phys. Chem.*, 18, pp. 355–371, 1914; Bancroft, W. D., "Applied Colloid Chemistry," pp. 90–128, 1921.

[33] Gruner, J. W., ECON. GEOL., 17, p. 431, 1922.

[34] Lovering, T. S., *op. cit.*, p. 528.

[35] Clark, F. W., *op. cit.*, pp. 110–111.

Weiss [36] has shown that peat solutions can change an impure clay to a residue of almost pure kaolin. Gruner [37] determined the solvent action of peat solutions on pyrite, hematite, limonite, siderite, magnetite, augite, olivine rock, serpentine, glauconite sand, greenalite rock, magnetic ferruginous chert, Ely greenstone, Duluth gabbro, and Sudbury nickel ore. He concluded that solutions from decaying plants dissolve all oxides and carbonates of iron and most of the silicates, but they do not appear to attack pyrite appreciably. In peat solutions in contact with air a smaller quantity of iron and silica is taken into solution. It is possible that this quantity is all in the colloidal state.

The work of the various investigators shows that carbonic acid and solutions from decaying organic matter are among the most powerful solvents of iron and silica in nature and to a lesser extent pure water and oxygenated water are effective. The conclusions, however, as to which agent is the most powerful are contradictory. In order, if possible, to decide this question and also to see if coarse and fine grinding would have any appreciable affect on the solvent action of the various reagents a series of experiments was carried out.

The rocks chosen for the solution experiments were norite and diabase. They were collected by Mr. G. B. Tribble from the Sudbury district, Ontario. The specimens of norite contained appreciable amounts of sulphides, whereas the samples of diabase were practically free from them. Each of the samples was divided into two portions; the norite fractions being ground to 10- and 48-mesh and the diabase to 48- and 150-mesh. One set of experiments consisted of placing 100 grams of 10-mesh norite in each of four winchesters, then adding 2000 cc. of distilled water. Carbon dioxide was then passed through one bottle for 24 hours and oxygen through the other. To the third bottle was added 100 grams of peat that had been obtained from the Holland river, Holland Landing, Ontario, and had been allowed to dry for three months at room temperature. The fourth bottle contained only the sample and distilled water. This procedure

[36] Weiss, F., *Zeit. Prakt. Geol.*, p. 365, 1910.

[37] Gruner, J. W., ECON. GEOL., 17, pp. 422–436, 1922.

was followed, also, with the 48-mesh norite and the 48- and 150-mesh diabase.

At the end of 70 days, 500 c.c. of solution was drawn off from each winchester, and evaporated. The organic matter was then burned off and the residue analyzed by standard methods (silica by hydrofluorizing and iron by titration with potassium dichromate). The carbonated and oxygenated solutions were re-treated with carbon dioxide and oxygen, and together with the other solutions were set away for 287 days, when 500 c.c. of solution was again drawn off from each and analyzed as before. A blank experiment was carried out to determine the quantity of silica and iron taken into solution from the container. The results were calculated as parts per million silica and Fe_2O_3, and they are given in Table IV.

The results shown in Table IV. indicate that carbonated water is the most effective solvent of silica and iron from norite and diabase, that peat solution is the next most effective solvent, distilled water the next, and oxygenated water the least of the solvents used. In the case of distilled water and oxygenated water relatively little iron is taken into solution; the proportion of silica, however, is considerably higher. For 70 days, the finer a sample was ground the greater was the rapidity with which it gave up its iron and silica but at the end of 287 days this relation did not hold so well, especially with regard to the amount of silica taken into solution from the diabase by distilled water, peat solution, and carbonated water. The explanation may be found in the fact that the various solutions were agitated every 7 days for the first 70 days, whereas for the remaining 217 days, they were allowed to remain undisturbed. The diabase, being ground the finest, was able to settle to a dense, compact mass on the bottom of the winchester, thus permitting less circulation of the solutions than in the more coarsely ground rock powders.

The norite, with carbonated water, yielded, in the given time, a far higher percentage of iron than the diabase, irrespective of the mesh to which the samples were ground. This difference may possibly be due to the norite containing more sulphides of

TABLE IV.

SOLUTION OF SILICA AND IRON FROM NORITE AND DIABASE.

(Parts per million.)

Rock	Mesh	Solutions															
		Distilled water				Distilled water and peat				Oxygenated water				Carbonated water			
		Time in contact with rock				Time in contact with rock				Time in contact with rock				Time in contact with rock			
		70 days		287 days		70 days		287 days		70 days		287 days		70 days		287 days	
		SiO_2	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2	Fe_2O_3
Blank		1.6	0.2	1.9	0.4	1.6	0.2	1.9	0.4	1.6	0.2	1.9	0.4	1.6	0.2	1.9	0.4
Norite	10	7.0	0.6	14.4	0.8	54.4	5.2	51.0	5.0	5.6	0.6	10.0	1.2	65.6	12.0	78.4	27.2
Norite	48	9.4	1.6	20.4	1.6	66.0	8.8	52.0	7.6	6.2	0.8	13.6	1.5	73.8	36.4	89.2	45.8
Diabase	48	6.0	0.4	16.0	1.2	40.8	7.2	45.2	8.0	5.4	1.1	9.8	2.0	46.8	7.6	54.2	9.4
Diabase	150	10.2	1.2	15.2	0.9	47.4	12.0	47.2	12.8	7.2	1.8	14.2	1.4	51.4	11.2	50.0	11.8

iron, which yield readily to the action of carbonic acid. Possibly, also, the sulphides may have broken down, yielding sulphuric acid, which in turn may have dissolved more iron.

A feature that is difficult to account for is, that increasing the time of contact of the peat solution with the rock, instead of causing an increase in the dissolved iron, affected practically no change and even a slight decrease. The results obtained by Gruner [38] show this peculiarity in a still greater degree. A possible explanation is that a portion of the iron in solution, due to the great excess of organic matter, is changed to carbonate and, as such, precipitated.

The relative solvent action of carbonated water and peat solution was determined for bog iron ore. In each of two winchesters were placed 100 gms. of bog iron ore, and 2000 c.c. of distilled water. The ore was obtained from the banks of the creek flowing out of Calumet Lake, Quebec. To one winchester was added 100 gms. of dried peat, and through the other carbon dioxide was passed for one week. At the end of this time both solutions were analyzed for silica and iron. The carbonated water dissolved 6.84 parts per million silica and 4.21 parts per million iron, calculated as ferric oxide, whereas the peat solution dissolved 2.4 parts per million silica and 5.6 parts per million iron, calculated as ferric oxide. Thus it appears that carbonated water is a more effective solvent of silica from bog iron ore than is peat solution. On the other hand, peat solution appears to be the better solvent of iron. This difference may be due, as Gruner [39] points out, to the peat having the power to reduce ferric iron compounds to the ferrous state, thus transforming them into a much more soluble form. Organic acids also play a part. Inorganic acids, under exceptional circumstances, may have caused much iron and silica to go into solution.

MANNER OF TRANSPORTATION OF IRON.

Beck,[40] in his discussion of the origin of lake and bog ores, states that the iron might be carried by the streams as sulphate,

[38] Gruner, J. W., ECON. GEOL., 17, p. 427, 1922.

[39] *Idem*, p. 435.

[40] Beck, R., "The Nature of Ore Deposits," 1, pp. 101–103, 1905. Van Hise, C. R., U. S. Geol. Surv. Mon. 47, p. 550, 1907.

bicarbonate, and salts of organic acids such as humus acids. Van Hise and Leith [41] think that iron may be carried as a ferrous salt of silicic, carbonic, sulphuric, hydrochloric, or other acids. Clark [42] believes that iron, in general, is transported as ferrous carbonate. Hayes,[43] in his study of the formation of the Wabana ores of Newfoundland, points out that the iron was transported by the streams as salts of mineral and vegetable acids, such as organic salts, chlorides, sulphates, and ferrous bicarbonate. Dole,[44] in calculating the error of combining values in water analyses, treats the iron and aluminium as bases in waters containing free mineral acids and as colloidal in all other waters. Aschan [45] indicates that iron may be carried as soluble ferrihumates and ferrohumates. Harder [46] believes the supposition to be fairly well founded that iron is carried in solution in natural waters principally as the bicarbonate, or at least as a soluble carbonate, for iron is found in solution in many waters in which there is no radicle present except the bicarbonate. Gruner [47] suggests that as iron, with the possible exception of a fraction of one part per million, is precipitated from surface waters unless organic matter is present, it is quite probable that larger amounts are carried as organic colloids, or adsorbed by organic colloids, and not as bicarbonate.

From a perusal of the literature it is evident that the chemical state in which iron is transported in natural solution is still open to question. The suggestion is here made that the greater portion of the iron carried in natural waters high in organic matter is in the condition of a ferric oxide hydrosol stabilized by the organic colloids in the water, and that smaller quantities are carried as salts of organic and inorganic acids.

The following experiments give very good evidence in support of this suggestion:

[41] Van Hise, C. R., and Leith, C. K., U. S. Geol. Surv. Mon. 52, p. 515, 1911.
[42] Clark, F. W., U. S. Geol. Surv. Bull. 770, p. 65.
[43] Hayes, A. O., Canada Geol. Surv. ser. 66, Mem. 78, pp. 71–76.
[44] Dole, R. B., U. S. Geol. Surv. Water-Supply Paper 236, p. 33, 1909.
[45] Aschan, O., *Zeit. Prakt. Geol.*, 15, pp. 56–62, 1907.
[46] Harder, E. C., U. S. Geol. Surv. Prof. Paper 113, p. 71, 1919.
[47] Gruner, J. W., ECON. GEOL., 17, p. 445, 1922.

(1) A 500 c.c. sample of water from Fox creek, Niblock, Ontario, containing 11.7 parts per million organic matter and 8.6 parts per million ferric oxide, was placed in a flask, and oxygen was bubbled through it for a week. On analysis it was found that 5.5 parts per million ferric oxide still remained in solution. This iron could not be detected in the solution except after the addition of a highly ionized acid. It appears, therefore, that the iron is in the colloidal form and is not present as bicarbonate.

(2) Two 50 c.c. samples of solution were obtained in which 48-mesh norite had been in contact with carbonated water for 70 days. The bicarbonate solutions contained 36.4 parts per million iron, calculated as ferric oxide. To one of the 50-c.c. samples was added one c.c. of peat solution containing 922 parts per million organic matter. Thus the total reaction mixture of 51 c.c. contained approximately 36 parts per million iron, calculated as ferric oxide, and 16 parts per million organic matter. The two samples were placed in the steam bath in order to rapidly drive off the carbon dioxide. At the end of one hour the samples were examined and it was found that the one to which the peat solution had been added was still clear and showed no indication of a precipitate, whereas a yellowish brown, quite dense precipitate of ferric hydroxide had appeared in the tube containing no peat solution. Similar results were obtained by bubbling air through the solutions for three days instead of treating in the steam bath. This result was to be expected, for Gruner [48] found that air, without agitation of the solution, precipitated all the iron in three days from solutions containing iron bicarbonate formed by the action of carbonic acid on minerals and rocks.

This experiment shows very conclusively that as much as 36 parts per million ferric oxide can be held in solution by 16 parts per million organic matter. The iron cannot be in solution as bicarbonate, for boiling or aeration would have precipitated it, as in the case of the sample that contained no organic matter. The stabilized sample gave no test for ferrous or ferric iron with potassium ferricyanide and potassium ferrocycanide. The only

[48] *Idem*, p. 436.

explanation that suggests itself is that the iron in solution as bicarbonate on losing its carbon dioxide became very finely divided ferric oxide, which was stabilized by the organic colloids of the peat solution. The iron, therefore, had been changed from a true solution of ferrous bicarbonate to a ferric oxide hydrosol.

These experiments seem to indicate that sufficient stress has not been laid on the possibility of iron being transported as a ferric oxide hydrosol in natural waters containing organic matter.

Since these experiments were carried out a paper by Gill on the "Origin of the Gunflint Iron Bearing Formations" has come to hand. From field evidence Gill [49] concludes that the iron going to make up the Gunflint formation was derived from the land and transported by rivers to the basin of deposition as a colloid stabilized by protective agents such as organic matter. It appears that at times the greater portion of the iron was transported as a ferric oxide hydrosol, while at others it was carried as a ferrous silicate hydrosol, for he points out that one bed may consist almost entirely of hematite granules while beds above and below it consist essentially of greenalite granules.[50]

Gill's conclusions, in so far as ferric oxide hydrosols are concerned, are in accord with the experimental evidence given above and are in agreement with the views of the authors. It may not be advisable, however, to say that much iron is in solution as ferrous silicate sol until further experimental evidence is accumulated.

Summary.

1. Iron is not carried as bicarbonate in natural surface solutions high in organic matter, but in all probability it is transported as a ferric oxide hydrosol stabilized by organic colloids.

2. A relatively small quantity of iron may be carried as salts of organic acids or adsorbed by organic colloids.

3. As much as 36 parts per million ferric oxide, formed by the oxidation and hydrolysis of ferrous bicarbonate, can be held in colloidal solution by 16 parts per million organic matter.

[49] Gill, J. E., ECON. GEOL., 22. p. 725, 1927.
[50] *Idem*, p. 702.

4. Under exceptional conditions iron might be in solution in surface waters as salts of inorganic acids and as a ferrous silicate hydrosol.

5. It is concluded that the iron going to make up large sedimentary iron formations was transported principally as a ferric oxide hydrosol, stabilized by organic matter.

TRANSPORTATION OF SILICA.

Silica is generally transported in natural waters as a colloid and not as acid ions. It is not possible for the silicates of the alkalies to exist as such at dilutions found in most natural waters.[51] Kohlrausch[52] pointed out in 1893, that in dilute solutions of sodium silicate hydrolysis has taken place to a considerable extent and Kahlenberg and Lincoln[53] state that complete hydrolysis of sodium silicate takes place at a dilution of 1257 parts per million silica. Dienert[54] believed that silica is carried in solution as alkaline silicate and that on separation of the alkali the silica is thrown down. More recently Bogue[55] found that complete hydrolysis of sodium silicate does not take place until dilutions very much lower than those indicated by Kahlenberg and Lincoln are reached. Wallace, Baker and Ward[56] show that the silica in the water of the Red river "is colloidal to the extent that one-sixth of the silica content can be separated by a supercentrifuge running at 40,000 revolutions per minute." The authors found that complete hydrolysis of sodium silicate does not take place until a dilution of at least 25 parts per million silica is reached. This observation is in accord with the results obtained by Bogue.

It would appear, therefore, that silica in solution in natural waters is transported as a true colloid provided the concentration does not exceed 25 parts per million, but if the concentration is

[51] Clark, F. W., *op. cit.*, 195.

[52] Kohlrausch, F., *Zeit. Physik. Chem.*, 12, p. 773, 1893.

[53] Kahlenberg, L., and Lincoln, A. T., *Jour. Phys. Chem.*, 2, p. 77, 1898.

[54] Dienert, M. F., *Bull. Soc. Chem.*, 4th ser., 13, pp. 381–394, 1913.

[55] Bogue, R. H., *Jour. Amer. Chem. Soc.*, 42, p. 2575, 1920.

[56] Wallace, R. C., Baker, W. F., and Ward, G., *Trans. Roy. Soc. Canada*, Sec. 4, p. 166, 1926.

higher it is possible for a small part to be transported as alkaline silicate. The average silica content of the rivers and lakes of the world does not exceed 15 parts per million.[57]

UNIVERSITY OF TORONTO,
TORONTO, CAN.

[57] For a full discussion see section on the precipitation of silica.

(*To be continued in next number*)

MARCASITE IN THE CONTACT METAMORPHIC ORE DEPOSITS OF THE TWIN BUTTES DISTRICT, PIMA COUNTY, ARIZONA.

BENJ. N. WEBBER.

The Twin Buttes district is in Pima County, Arizona, about thirty miles southwest of Tucson. The Twin Buttes deposits are of contact pneumatolytic type and occur on or near the contact between Carboniferous limestone and an intrusive orthoclase biotite granite that contains considerable pyrite in veinlets and as

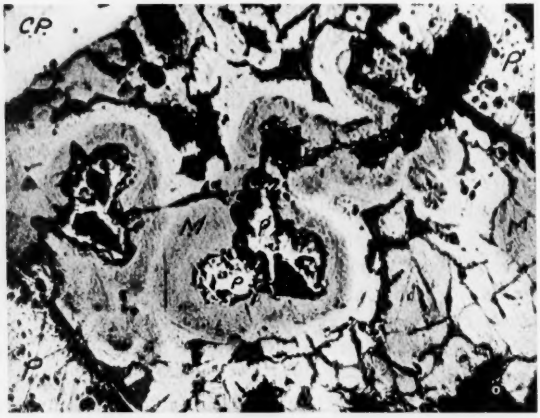
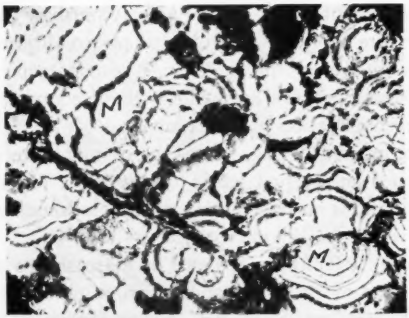


FIG. 1. M = marcasite; P = pyrite; CP = chalcopyrite; dark portion = gangue.

disseminated crystals. The metamorphism along the contact has been intense, as is indicated by the abundance of garnet and pyroxene together with considerable epidote and magnetite. The ore as mined at present consists of pyrite and chalcopyrite and

shows under the microscope no evidence of supergene alteration. An unexpected result of the study of this ore was the detection of marcasite.



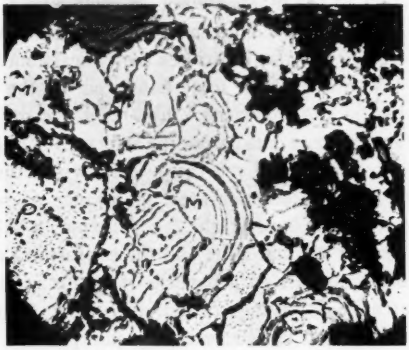


FIG. 2 (above). *M* = marcasite; dark portion = gangue.
FIG. 3 (below). *CP* = chalcopyrite; *M* = marcasite; *P* = pyrite; dark portion = gangue.

The intensely metamorphic character and general high temperature aspect of the deposits together with the almost total lack of supergene alteration make the occurrence of marcasite unusual, for, under ordinary conditions, marcasite is usually deposited

from cold acid solutions, and consequently in this type of deposit should be confined to the oxide or supergene alteration zone. Pyrite, on the other hand, is usually deposited by thermal or hot alkaline solutions and may be generally considered as hypogene in origin. Marcasite, as shown by Allen, Crenshaw and Johnson,[1] at a temperature of 450° C. and the proper conditions of acidity, will go over into pyrite but the change is monotropic, and pyrite can not be converted into marcasite without complete disintegration and a recombination of the atoms.

It is then apparent that the presence of marcasite in these deposits indicates an unusual set of conditions. The marcasite is not abundant and is noticeable only when a polished section of the ore is observed under the microscope.

Fig. 1 shows a typical occurrence of marcasite as a concentric structure around pyrite. The photomicrograph suggests that the marcasite has replaced the pyrite. Fig. 2 shows the typical concentric structure of the marcasite but no replacement phenomena. The veinlet of calcite crossing the marcasite shows that the marcasite is older. Fig. 3 also illustrates the typical concentric structure of the marcasite and to some extent shows the embayment of chalcopyrite in the marcasite. Fig. 4, a sketch, shows that some of the chalcopyrite cuts across the structure of the marcasite. An isolated development of marcasite is shown at the lower left of the figure, and the disintegrated appearance of some of the pyrite is shown at the lower right. Fig. 5, also a sketch, shows the development of the marcasite and the conformity of its structural lines to the outlines of a particle of pyrite. This indicates that the marcasite is younger than the pyrite. The relations sketched in Fig. 6 can not be so clearly interpreted. They may indicate the replacement of pyrite or merely the filling of a cavity in the pyrite by secondary marcasite.

DISCUSSION.

From the large amount of pyrite in the ore deposits of this region it is evident that the original solutions were hypogene

[1] Allen, E. V., Crenshaw, J. L., Johnson, J., "The Mineral Sulphides of Iron," *Amer. Jour. Sci.*, 4th Ser., vol. 33, p. 234, 1912.

and alkaline and the intensity of the contact action would indicate that the temperature was higher and the chemical action more intense than prevailed during the formation of most contact meta-

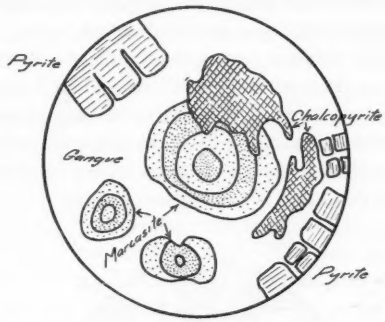


FIG. 4. Sketch showing chalcopyrite cutting across the structure of the marcasite.

morphic deposits. The temperature of formation of marcasite is generally understood to be not higher than 450° C. The formation of marcasite is not only determined by temperature, but is

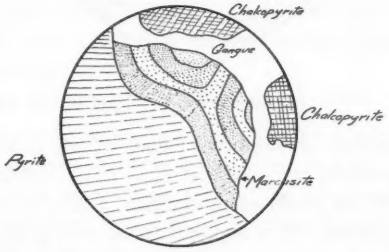


FIG. 5. Sketch showing development of the marcasite and conformity of its structural lines to the pyrite.

conditioned by the acidity or alkalinity of the solution. In this case even if the marcasite formed at a temperature above 450° C. the probable alkalinity of the solutions would have been in-

hibitive. It is therefore improbable that the marcasite formed at the initial phase (pneumatolytic) of contact action.

The usual occurrences of marcasite, aside from those that are probably due to the combination of organic iron and organic sulphur, are in superficial veins and oxidized ore zones. Since there has been little or no supergene action on these ores, the formation of marcasite in its usual manner from cold acid solutions is extremely unlikely. The ore body has never been penetrated to any extent by vadose solutions and the secondary or oxide zone minerals are completely lacking. It is therefore improbable that the marcasite was deposited by supergene solutions.

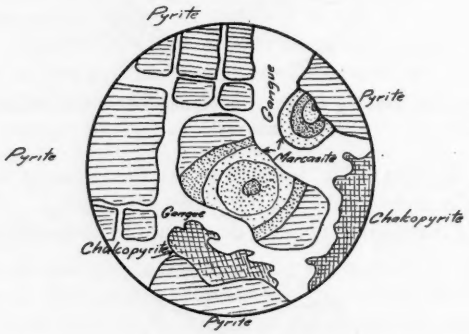


FIG. 6. Sketch showing relations of pyrite and marcasite.

The elimination of these two phases of ore deposition as the production phase of the marcasite leads to the consideration that the marcasite was produced by chemical action in some third or intermediate phase. It is suggested that during the later phase of hydrothermal action, at which time the chalcopyrite was probably formed, the alkalinity of the ore-bearing solutions may have been neutralized by action with the adjacent mass of limestone.

That the chalcopyrite and marcasite are close if not contemporaneous in deposition is indicated by their association. The penetration of a marcasite structure by a mass of chalcopyrite

indicates either crystal interference at the time of deposition, or replacement. If the latter took place it is an indication that one or the other was in solution at the time. This could have occurred at the time of deposition and would indicate that they were close in paragenesis, for the general associations would indicate that deposition of the chalcopyrite was preceded only by that of pyrite. That the solutions of hypogene origin were rich in iron is indicated by the presence of considerable magnetite in the ore deposit. In the formation of chalcopyrite by the action of a copper salt in solution on the pre-existing pyrite, both sulphuric acid and iron sulphate would be evolved. The sulphuric acid so formed would tend to neutralize any remaining alkalinity of the ore body and might even make it acid. The ores are highly ferruginous and a source of the iron of the marcasite is not hard to find; either the iron sulphate released by the pyrite during conversion to chalcopyrite or the iron present along the contact was available. The temperature at this time had probably fallen within the range of formation of marcasite. With an acid or neutral condition, a temperature not too high, and iron present as the sulphate, there would be necessary only the presence of some reducing agent to bring about the formation of marcasite. What this reducing agent may have been is unknown but the suggestion is offered that it might have been carbon dioxide evolved from the limestone.

CONCLUSIONS.

1. The formation of marcasite at the pneumatolytic stage of contact metamorphosis is extremely unlikely, as both the temperature and alkalinity would have assured the formation of pyrite. Had the marcasite been deposited at this stage it would have been present in much larger quantity.

2. The formation of marcasite by the action of cold acid vadose solutions is precluded by the fact that there has been no action of supergene or vadose solutions on the deposit.

3. It is suggested that the formation of marcasite took place at an intermediate stage and was due to a lowering of the temper-

ature and a change from an alkaline to a neutral or acid condition consequent upon the formation of chalcopyrite from pyrite.

ACKNOWLEDGMENT.

The writer is indebted to Dr. F. L. Ransome, who kindly read and criticized the manuscript.

1218 EAST CULVER ST.,
PHOENIX, ARIZ.

ZONING IN MICHIGAN COPPER DEPOSITS AND ITS SIGNIFICANCE.

T. M. BRODERICK.

PART II.

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INTRODUCTION.

In the many years of geological work in the Michigan copper district little or nothing was found pointing to zoning. Occasional statements have been ventured that arsenic increased and that analcite, silver, and sulphides decreased in depth. Some of these statements have proved to be correct, others have not. However, nothing at all definite had been found indicating any change in types of minerals in the thousands of feet of lodes opened from the surface downward. This was recognized by students of economic geology who attempted to explain the genesis of these ore bodies as being somewhat of an objection to the theory of formation by ascending magmatic solutions after the beds assumed essentially their present position. It is not that

zoning has not been looked for. The writer knows that it has been continually in mind during mineralogical studies of the district. The difficulty has been that the changes have been too gradual to be detected readily in a study of any one mine or lode, and that no one has had any scheme by which widely separated deposits could be placed in their proper relative positions above or below each other.

It has always been accepted that certain mines or lodes had their own mineralogical characteristics. The Copper Falls mine had an abundance of adularia, datolite, and zeolites. The Osceola lode had adularia, datolite, and prehnite. The Isle Royale and Baltic lodes had sericite, ankerite, sulphides, and arsenides. Types of rock alteration likewise are different in different mines. The inclination has been to regard these as simply mineralogical peculiarities of the various lodes. However, it will be brought out that these mineralogical associations instead of being peculiarities of the lodes are peculiarities of the zones in which the portions of the lodes which we observe occur.

ZONAL RELATIONSHIPS OF LODES AS DETERMINED BY ARSENIC RATIOS.

If the arsenic curve, the development of which was explained in the preceding paper, is correct, the various mines and lodes are thereby placed in approximately their proper relationship to each other in depth along the lodes. It thus furnishes us with an invaluable method of studying zoning.

Fig. 4 is based upon Fig. 3, showing progressive changes in arsenic ratios. If now the construction of the arsenic ratio curve is correct in showing the depth relations of the various lodes, and if there is any zoning in the district, the lodes having similar mineralogical associations and types of rock alteration should be grouped together, and those features indicating higher temperatures should characterize the deeper zones.

Certain minerals extend throughout the entire zonal range of from 20 to 30 thousands of feet. These are epidote, quartz, calcite, pumpellyite, chlorite, and native copper. They may be

called the "persistent" minerals, whereas those that do not extend throughout the diagram are characteristic of certain depths or zones and will therefore be referred to as "characteristic" minerals.

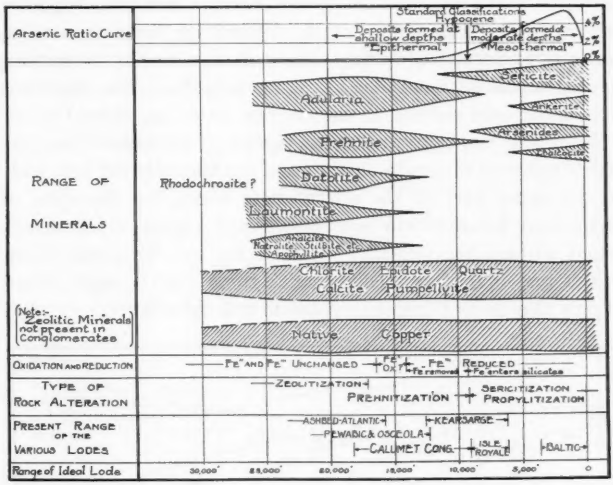

FIG. 4. Zonal ranges of the lode deposits and their various chemical and mineralogical features.

Characteristics of Deep Zones.[4]—The Baltic lode is characterized by sericite, ankerite, and in places by chalcocite and copper arsenides in the lode itself. The rock alteration accompanying the copper is a bleaching characterized by epidote, pumpellyite, and chlorite. Chemically it means a reduction of much of the ferric iron of the original lode to ferrous iron which enters the pumpellyite and chlorite. The normal red lode is turned green around the copper.

The Isle Royale lode has much the same characteristics mineralogically and chemically. Sericite, arsenides, ankerite, and sul-

[4] The terms Deep, Intermediate, and Shallow as applied in this discussion to the local zoning in Michigan are simply relative and do not refer to similar terms as used in the standard classifications of ore deposits.

phides are present, although the latter two less abundantly than in the Baltic lode.

Characteristics of Intermediate Zones.—Portions of the Kearsarge Amygdaloid and the Calumet Conglomerate ore bodies are examples of the intermediate zones. Sericite, ankerite, sulphides, and arsenides decrease. Potash, instead of entering sericite, forms orthoclase or adularia. The rock alteration accompanying the copper differs from that of the lower zones in that the ferric iron is not only reduced to the ferrous state, but instead of remaining and entering into ferrous silicates it is more or less completely removed causing a bleaching of the normally red lode rock. In the upper part of the intermediate zones the alteration of ferric iron becomes less pronounced and copper is commonly found without the bleaching characteristic of the lower zones. In this respect the intermediate zones grade into the upper zones, as they also do by increase in prehnite and datolite.

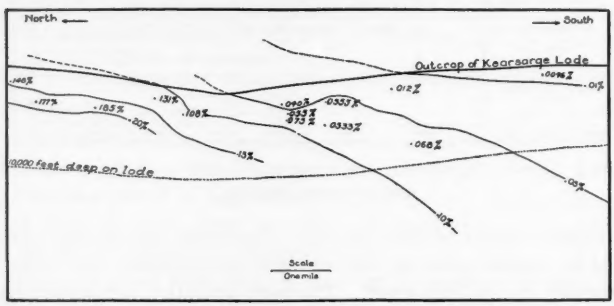

FIG. 5. Zoning on the Kearsarge Amygdaloid as brought out by lines of equal arsenic ratio.

The Kearsarge lode is of great interest in the zoning study. It will be noted that it occupies an intermediate position overlapping the higher zones such as the Osceola and Pewabic on the one hand, and the lower zones as the Isle Royale on the other. A plan of the lode showing the various arsenic ratio determinations brings out the zoning nicely (Fig. 5). Lines of equal arsenic ratio have been drawn. Coming south, prehnite, analcite, and datolite increase in amount as the arsenic ratio decreases. Many

specimens of Kearsarge lode from this less arsenical portion would be accepted as typical Osceola lode of the upper zones rather than Kearsarge lode. Northward, these minerals decrease and the orthoclase, epidote, calcite, chlorite, and pumpellyite of the more typical Kearsarge lode remain. In the vicinity of certain strong fissures which commonly contain arsenides of copper, the lode is sericitized and chloritized (Fig. 6). Ankerite is found

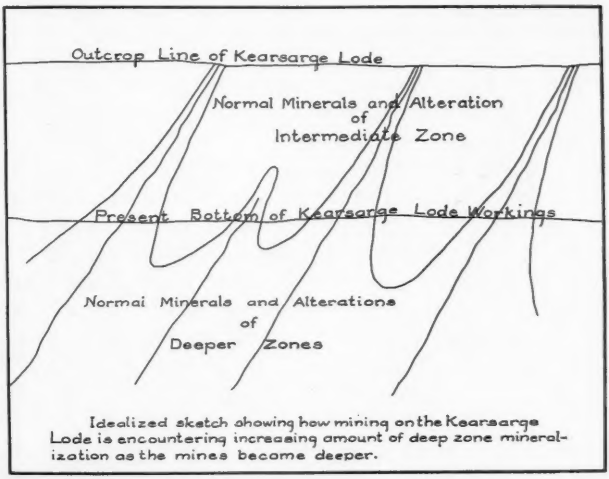
Outcrop Line of Kearsarge Lode
Normal Minerals and Alteration of Intermediate Zone
Present Bottom of Kearsarge Lode Workings
Normal Minerals and Alterations of Deeper Zones
Idealized sketch showing how mining on the Kearsarge Lode is encountering increasing amount of deep zone mineralization as the mines become deeper.

FIG. 6. Idealized sketch showing how deep-seated fissures intersecting a lode locally introduce abnormally deep type of mineralization.

also in the fissures and to some extent in the adjacent lode. These fissures are regarded as bringing up solutions from great depths, short-circuiting the strongly arsenical solutions which would otherwise be forced to find their devious way upward in the highly oxidizing environment of the lodes themselves. Thus, in the fissures and in the lode adjacent to them we find a type of mineralization and rock alteration characteristic of much lower zones, in a horizon normally of a much higher (or cooler) type of mineralization. There seems to be a decided tendency for

these areas to become more extensive in depth on the Kearsarge lode, so that gradually the deeper parts of the Kearsarge are taking on a chemical and mineralogical nature more and more characteristic of the Baltic-Isle Royale zone.

Thus we have the Kearsarge lode in an intermediate zone. In its shallow and southerly low arsenical portions it resembles the higher zones, and in its deeper more arsenical portion it resembles the lower zones.

Characteristics of Shallow Zones.—The Osceola and Pewabic amygdaloids have practically no sericite, ankerite, sulphide, or arsenide (Fig. 4). As in the intermediate zones, the potash, instead of going into sericite as it does in the lower zones, forms orthoclase and adularia. Datolite and prehnite are abundant. In some of the old mines in the upper part of the series, such as the Copper Falls and Arnold on the Ashbed lode, zeolites and zeolitic minerals including apophyllite, analcite, natrolite, stilbite, and laumontite occur in addition to prehnite, datolite, and adularia. These may represent even a higher zone than the Osceola and Pewabic. It is not easy to decide on the basis of arsenic ratio as that is so low that analytical error is greater than the differences between them. The solutions in this zone apparently had lost some of their power to reduce the ferric iron of the lodes because the bleaching surrounding the copper in the Pewabic and Osceola lodes is not nearly so common as in the lodes of the lower zones. What bleaching there is, however, is of the iron-removal type characteristic of the intermediate zones.

Overlapping of Zones.—Just as it is possible to get lower zones short circuited up into the higher zones by strong fissure channelways, so it is possible to get the minerals of higher zones into the lower zones during the waning activity of the solutions. Thus, in all of the zones late fissures and the interiors of vugs may have laumontite, prehnite, and datolite deposited in them. Such occurrences in the lower zones are regarded as being the result of the final cooler solutions, and it amounts to a recession of the zonal deposition downward. If such an explanation is correct, then a similar *advance* of the zones to greater and greater

distances from the magmatic source at the beginning of the mineralization period suggests itself as a possibility. In this connection specimens from arsenide fissures in which the arsenide shows casts of prehnite, which is now practically never found in arsenide fissures, suggest that the fissures were filled with prehnite at an early stage in the mineralization, before things really became warmed up, and that later the arsenides were deposited, in some cases around the prehnite which, no longer stable in the hotter environment, was removed. This short circuiting of lower zones into horizons normally higher and the recession of the conditions permitting higher zone minerals to be deposited in the lower zones toward the end of the mineralization period, is probably partly responsible for the long delay in recognizing the zoning in the district.

Zoning of Other Constituents.—There are other mineralogical and chemical constituents of the deposits which undoubtedly have a zonal distribution, but the data are not at hand to place them properly in the diagram. Thus, the small amounts of silver, nickel, and cobalt, and such minerals as the sulphates probably have definite ranges. There is an abundance of partial silver assays which will be studied in the near future. It is to be noted that this is a district whose production consists almost entirely of one metal. Thus, we cannot speak of the copper zone in relationship to the zones of other metals, but must speak of the prehnite zone, or the adularia zone, or the zones of sericitization, zeolitization, iron oxidation, or iron reduction. The ratio of sulphur to copper apparently increases in the lower horizons, much as the arsenic does.

ZONING IN FISSURES.

The rocks of the district are cut by numerous fissures that contain a variety of types of mineralization. Thus there are fissure veins characterized by mass copper, arsenides, sulphides, datolite, prehnite, quartz, calcite, laumontite, and ankerite. There are those which chloritize the adjacent country rock and those that redden it. Some thoroughly sericitize it and others equally strong

in appearance do not seem to affect it. There are even fissures heavily mineralized with manganese minerals. Some of these fissure veins have a type of mineralization belonging to higher zones than nearby amygdaloid mineralization, others lower zones, and still others have minerals of the same zone as the surrounding ore bodies. Without the guide of the arsenic ratios of the lodes to establish the characteristics of the zones, the fissure veins with their great variety seem hopeless. Having established the type minerals of the various zones by means of arsenic ratios, it is easy to apply the same classification to the fissure veins.

The general rule seems to be that lodes of all zones are cut by three types of fissure veins (Fig. 7); namely, first, deep pre-mineral, which short-circuited solutions of deeper zones into the normal lode environment (examples being the arsenide fissure veins that cut the Kearsarge lode); second, shallow pre-mineral, not reaching to great depths, therefore having about the same minerals as the nearby lode itself (examples, many of the stronger non-persistent fissure veins); and, third, fissures formed or re-opened late in the mineralization period, after things became cooled off. Most of the laumontite-prehnite fissure veins which occur in all zones and all amygdaloid lodes are of the latter type. The following discussion can be most readily understood by referring to Fig. 7.

Considering only the strong pre-mineral fissures and disregarding the later and generally weaker fissures, we find that lodes of the upper zones are cut by fissure veins having the same type of minerals as the lodes themselves or of a somewhat deeper type. Thus, the Ashbed Amygdaloid is cut by mass copper veins having the datolite, adularia, and analcite, which are characteristic of the Ashbed itself. These fissure veins did not affect the adjacent rock or included fragments to any great extent. The Ashbed is also cut by the prehnite-calcite veins characteristic of intermediate zones.

Amygdaloids of the intermediate zones such as the Kearsarge are cut by mass copper fissures with the calcite-epidote gangue which is characteristic of the amygdaloid zone in which they

occur. The strong datolite fissure veins of the upper zones are not common although there are prehnite fissure veins. Some of

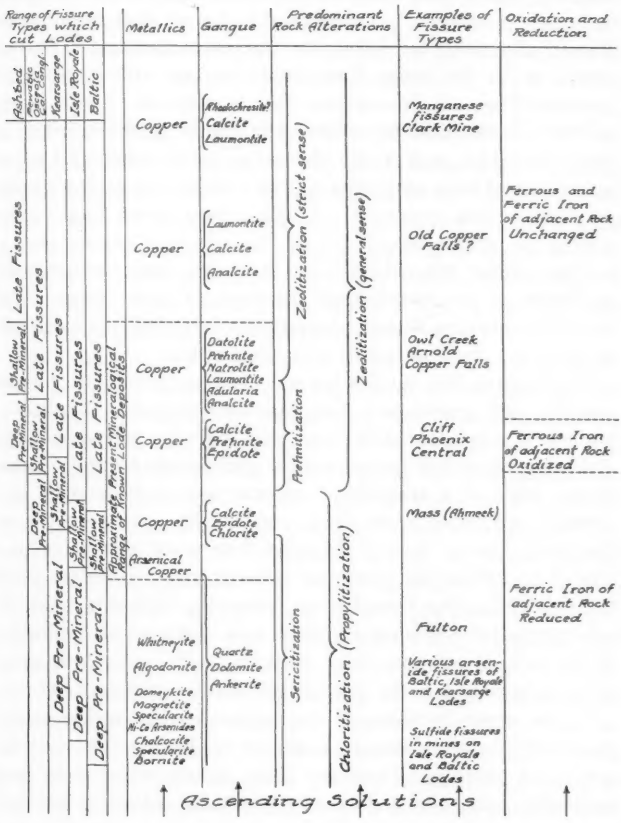

FIG. 7. Zoning in the fissure veins that intersect the lodes.

the fillings of these fissures had an oxidizing effect on the wall rock. However, in going northward into more and more arseni-

cal portions of the Kearsarge lode the fissure veins that cut the lode become more and more arsenical. The southernmost known arsenide fissure vein comes in where the lode arsenic reaches a ratio of .10 per cent. In this vein the lowest arsenide minerals, known collectively as whitneyite, are most abundant. Further north, as the Kearsarge Amygdaloid becomes still more highly arsenical there are fissures that contain minerals of still higher arsenic content; first algodonite with quartz gangue coming in, then domeykite, and finally domeykite with nickel and cobalt arsenides and some magnetite and specularite in a gangue of predominantly dark carbonate. All these deep-rooted fissure veins cutting the middle zone chloritize the lode rock nearby and, as has been stated, this chloritization is in some respects chemically equivalent to the normal rock alteration of lower zones. The arsenide-containing fissures also strongly sericitized the lode rock, an alteration characteristic of lower lode zones.

The fissures that cut the lower lode zones commonly contain arsenide with quartz, and dark carbonate gangue. In addition are found many chalcocite veins with ankerite and specularite, and in the Baltic lode they also carry considerable bornite. Some fissure veins of a transition type, carrying both sulphide and arsenide, are found in the Baltic and Isle Royale lodes. As we find many fissure veins in the upper lode zones that bring in a type of mineralization belonging to lower zones, so we are justified in believing that these fissures containing chalcocite, ankerite, and specularite, which cut the lower lode zones are an indication of the type of solution which traversed still deeper lode zones which lode mining in the district may not have yet revealed.

In the upper horizons of the copper-bearing series, stratigraphically above the important known ore bodies, numerous fissure veins outcrop. These are filled mostly with calcite and laumontite, with minor amounts of prehnite, adularia, and late and rarer constituents. At one place two veins with abundant manganese oxides probably derived from manganiferous carbonates, are known. These are usually referred to as something entirely out of place in the district. Perhaps they fit into the

zonal system as among the normal minerals of the higher zones.

Thus we may construct an ideal fissure vein for the Michigan copper district as we constructed an ideal lode (Fig. 7). It is to be noted that the zones represented by this fissure extend beyond the known lode deposit zones both at the top and at the bottom.

WHAT WILL BE FOUND AT GREATER DEPTHS IN THE LODES?

Although the mineralization and alteration effects of a strong fissure vein that crosses a lode reveal in many cases the effects of solutions normally belonging to a lower zone, and to some extent, therefore, may forecast the changes to be encountered in depth in lode mining, it is not considered possible at this stage of the investigation to predict what deeper mining on the lodes may reveal as to grade of ore except in a general way.

An arsenic ratio curve which probably portrays actual conditions has been constructed, showing a point of maximum arsenic deposition. Similarly, curves showing prehnitization, sericitization, chloritization, iron reduction, iron oxidation, and other mineralogical and chemical features might be constructed if we had sufficient quantitative data. Each of these would probably resemble the arsenic curve in showing a point of maximum deposition or reaction. Fig. 4 indicates crudely the zonal range of some of these features. Of prime importance would be the ability to construct a copper curve with its characteristics of rise, maximum and decline. All of these curves would probably bear a more or less fixed relationship to each other, and it might, therefore, be possible to deduce the position of a given lode on all of the curves, knowing its position on any one of them. Above all, it would be desirable to be able to say that the range of commercial copper deposition had a given distance relationship to some easily determinable feature. This is not yet possible, however. We know very little concerning the copper curve except that in so far as the arsenic curve is reliable, commercial deposits do occur over a range of probably 20,000 feet and more along the lodes. The point of maximum copper deposition may lie

outside the region included in the known commercial deposits. Even though we did know the shape and position of the ideal copper curve, the actual percentage of copper in the lode rock would be influenced by local features such as barriers, or constrictions and enlargements of the lode channels, that are known to have had a decided local influence on copper deposition. The Copper Range mines on the Baltic lode are advancing the frontiers of the knowledge of the mineral zones because they are at present getting into deeper zones than any of the other mines. Indications are that they are on the declining side of the arsenic ratio curve, but we do not know on which side of the copper curve they are operating.

It would seem, however, that this study does indicate that mines operating on commercial lodes having the characteristics of the higher zones are not going to lose their copper suddenly because they run into the bottom of the zone of copper deposition. Conceivably, certain structural features can cause the ore to become lower grade or even non-commercial at relatively shallow depths in such mines, but copper deposition probably continued for long distances below the present bottoms of the mines of the upper zones.

RELATIONSHIP OF ZONES TO GENERAL STRUCTURE.

Why do zones which are so far apart vertically outcrop at about the same elevation? Is it because there has been a widely differing amount of erosion over the different lodes, or is it because the source of solutions lies at different depths down the various lodes? The latter more probably expresses the facts. It is not intended at this time to discuss at any length the origin of these deposits as this subject is being covered elsewhere.[5] It is thought that the copper-bearing solutions were derived from an underlying magmatic source and that they ascended the permeable channels furnished by the tilted amygdaloids and conglomerates, altering the rocks and, where conditions were favorable, deposit-

[5] Butler, B. S. and Burbank, W. S., "The Copper Deposits of Michigan," U. S. Geol. Surv. Prof. Paper 144, 1929.

ing copper. That there is a great underlying intrusive is known from the surface outcrops which occur around the lower edges of the Keweenawan of the Lake Superior syncline. The largest outcropping mass is the Duluth gabbro with associated acidic differentiates in Minnesota, but in a similar geological position in Wisconsin and Michigan there are numerous smaller outcrops of the same types of rocks. The idealized section (Fig. 8) shows

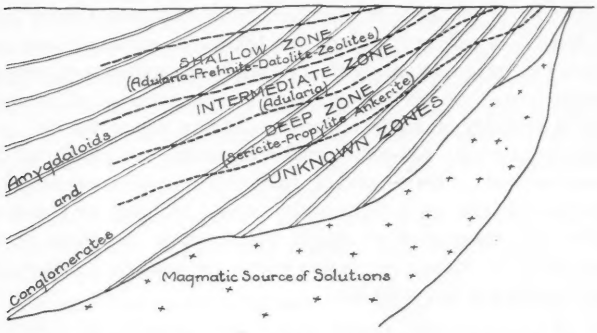

FIG. 8. Section showing hypothetical relationships of lodes, zones, and underlying magmatic solution source.

graphically the writer's idea of the explanation of the various zones outcropping at surface, the shallow zones occurring only in the higher horizons stratigraphically, whereas the deeper zones outcrop in the lower horizons, but are also to be found down the dip of the lodes whose outcrops are in higher zones.

QUANTITATIVE METHODS OF DETERMINING ZONING.

The writer is convinced that more quantitative methods of working out zonal relationships may be possible in many districts. In the present example the arsenic ratio curve, worked out by analyzing a mass of data already in existence, has led to an understanding of the relationships of the widely separated ore bodies, not only to each other but to the source in depth. It has also

contributed strong support to the hypogene theory of their genesis. There are undoubtedly many districts where a similar type of data is in existence, and which need only to be studied and correlated with the local geology to enable similar results to be obtained. The method of obtaining ratios between two constituents of the ore bodies, perhaps between two important metals, or between an important metal and a minor metal, or even between two minor metals, has one outstanding advantage; *i.e.*, its independence of the absolute quantity of the constituents being considered. A rich ore body or one below the economic limit can thus be studied equally well. A study of gold-copper, nickel-copper, molybdenum-copper, or silver-lead ratios, for instance, could probably be made in certain districts where the data are already at hand. Once the zonal relationships are established by such methods, a corresponding zoning of mineralogical constituents or of types of rock alteration would probably be found to exist, the recognition of which would enable the study to be carried on to include ore bodies where the quantitative chemical data might not be available.

SUMMARY.

By means of a study of the changes of the ratio of arsenic to copper in depth, it has been possible to place the widely separated lode deposits of native copper in a certain zonal relationship with each other. It is found that deposits grouped together because of occupying similar positions on the arsenic ratio curve also resemble each other in their mineral associations, oxidation and reduction reactions, and type of rock alteration. It is possible to predict what mineralogical changes are likely to occur in mining the various deposits to greater depths. Having thus determined the peculiarities of the various zones in which the lode deposits may be placed, it is possible to extend the zones beyond the known lode deposits by studying the characteristics of the various fissures which cut the lodes. The entire situation has been epitomized in Figs. 4, 7, and 8.

Genetic Classification of the Michigan Copper Deposits.

Deposits.

At the December, 1922, meeting of the Society of Economic Geologists, L. C. Graton, speaking for the Special Geological Investigation of the Calumet & Hecla Mining Company, pointed out that from the standpoints of possible source of metal bearing solutions, method of transportation, chemistry of deposition, mineralogy, and structural relationships, the evidence indicates that these deposits were formed after the beds had essentially assumed their present attitude by hot solutions ascending from a deep magmatic source. However, even the proponents of this theory recognized that their case would be considerably strengthened if the changes in depth, which extensive deposits of that type frequently show, could be recognized. This objection is removed by the foregoing discussion.

The deposits are commonly referred to as the "zeolitic" native copper deposits. Classifying prehnite and datolite among the zeolites, only 25 per cent. of the copper produced in the district has come from zeolitic deposits. If we exclude prehnite and datolite, and consider only those deposits characterized by the true zeolites, less than 1 per cent. of the copper has come from such deposits. The Calumet Conglomerate, which has produced 45 per cent. of the copper of the district, has practically no zeolites or zeolitic minerals. As pointed out by Singewald[6] in his comparisons of the Corocoro, Bolivia deposits and the Michigan deposits, zeolites are purely incidental to native copper deposition. They are not even present in some of the deposits such as the Calumet Conglomerate and Corocoro.

If the Michigan deposits are formed by hypogene solutions, the minerals and reactions at the lower end of the series, as established by the arsenic curve, should indicate higher temperature than those at the upper end (Fig. 4).

Referring to the text book descriptions of the characteristics of deposits of Intermediate Depth, we find that carbonates such

[6] Singewald, Joseph T., Jr., A Genetic Comparison of the Michigan and Bolivian Copper Deposits, Econ. Geol., vol. 23, no. 1, pp. 55–61, January–February, 1928.

as calcite, dolomite, and ankerite are common, that adularia and orthoclase are rare, zeolites never present, and that sericitization of the country rock where it is igneous is the principal alteration. Pyrite is said to be always present. Except for the last statement, the deposits of native copper in the deeper zones having an arsenic ratio greater than .1 per cent. have exactly these characteristics, and although pyrite is entirely lacking, it is significant that there is increasing sulphur in the lower zones.

Similarly, text book descriptions of the characteristics of deposits of the Shallow Depths state that siderite is rare, sericite not abundant, that adularia is one of the most widespread and characteristic of the gangue minerals, and that zeolites are in some cases present. These are some of the outstanding features of the native copper deposits of the upper zones having an arsenic ratio of less than .1 per cent.

Propylitization, an alteration developing chlorite, epidote, and pyrite, is common in deposits of Shallow and Intermediate Depths and is in many cases said to be an outer phase, surrounding the sericitization close to the veins. Except for the development of pyrite, which in these deposits is lacking, the chloritization in the lower zones accompanied by epidote and pumpellyite is the equivalent of propylitization and it bears a similar relationship to sericitization.

It would therefore seem that these deposits have most of the essential characteristics which are common to certain types of ore deposits the world over, and these characteristics place them in the class of hypogene deposits of the Shallow and Intermediate Depths (or the Epithermal and Mesothermal classes).

GEOLOGICAL DEPARTMENT,
CALUMET AND HECLA CONSOLIDATED COPPER CO.,
CALUMET, MICH.

EDITORIAL

EXPERIMENTS IN ORE GEOLOGY.

THE arrangements of ore studies have been such as to carry only small sectors of the basic problems to completion. Only a few small plots of ore-bearing ground have been put to critical scrutiny in the setting of all the sciences. Otherwise, both in the field and in the laboratory, such ground has been treated to the method of reconnaissance. The outcome of these arrangements is what would be expected. Taken in random, small samples, the available facts have been used by different schools of belief in favor of opposite conclusions. The recognized principles of today, like the "lateral secretion" of a generation ago, begin to look pallid and unreal. And, to emphasize this unreality after a half century of studies, the new ore districts continue to burst forth without warning.

These experiences have now created a disgust with reconnaissance and a demand for observation and experiment. It is true that we have no way of knowing in advance how far we shall ever be able to see. The position of ore in one locus rather than in another may have been fixed by some tiny factor, such as the incidence, at a certain time and point in the channel, of a single rock fragment, still remaining beyond the reach of our observations. And the origin of the metals may continue as a mere obscure detail in the complexities of earth-physics. Yet, whatever the present uncertainties, we know that our knowledge can be enlarged through the use of a method now available. The method is illustrated by the Zies-Allen-Merwin paper [1] on secondary copper enrichment. The field aspect of the

[1] Zies, E. G., Allen, E. T., and Merwin, H. E.: "Some Reactions Involved in Secondary Copper Sulphide Enrichment," ECON. GEOL. vol. II., pp. 407–503, 1916.

method is indicated in a current paper by Harrison Schmitt,[2] as follows:

"Impartial, detailed mapping often automatically solves many geologic problems through the completeness of the picture presented. Much less interpretation than is commonly used is necessary." . . .

Yet, despite the discontent, the availability of good method, and the resolve to do something different, the affair shows no definite sign of building up. Evidently, the observation and experiment must become systematic and comprehensive, and, therefore, abundant and irksome. In the place of reconnaissance must be substituted a deep invasion of every subject and every ore body, consuming years of effort on a single piece of vital ground. Where now we have a few appropriate workers, we shall need them by the score; and where now we have in America a single appropriate, working laboratory, and elsewhere only small scale operations in these particular subjects, we shall need laboratory equipment for pushing vigorously out into the higher temperatures and pressures and the more complex systems of ore-deposition.

In order to quicken the progress, how can we, then, better these arrangements? The proposal has been made that we better them through ample financing. But we may be certain that money cannot change the shape of the affair in any essential respect. We have no reason to hope that there are able investigators in large numbers waiting for financial encouragement to undertake these problems of ore-occurrence. Actually, there has, for a long time, been no lack of money, no lack of demand for guides to ore, and no lack of opportunity for anyone with ideas that would work. Fortunate, indeed, it would be, were the provision of money the principal need, and if we could put the blame for our condition on the dullness and ill-nature of capitalists; for, in that case, our salvation would come through the use of the ordinary, professional promoter. To fill the treasuries even to

[2] Schmitt, Harrison: "Extension of Ore Shoots, etc.," A. I. M. M. E. Tech. Pub. 164, p. 4, 1929.

overflowing would be a far simpler affair than to spend the money wisely.

It is, after all, not a question of getting money, but one of arousing a passion for the task in trained, intuitive workers. No mere opportunity for labor will develop that passion. Nor can men be appointed to the task. On the contrary, they must come in gradually, invited by its superior promise of a significant outcome. The first move to make toward enlarging experiment in ore geology is that of proving to the competent specialist that progress now seems possible. This would involve compiling all that we know and indicating all that we hope to accomplish.

The writer, therefore, recommends, as a stimulus to experiment in ore geology, a series of critical digests on subjects such as heavy metals in fresh rocks, the fluid carriers of heavy metals, the mechanics of ore-bearing cracks, and the limits in the usage of geological terms. These digests could not be forced out rapidly; they would be drawn out, gradually, from the hands of the several critics who are the masters of their individual subjects. If we propose to promote experiments in ore geology, costing high in money, energy and ability, our first effort must be to organize our activities through the preparation of such critical digests, which can be produced through facilities now existing. And, obviously, the beginning of this effort would be a digest of the critics themselves.

AUGUSTUS LOCKE.

DISCUSSION AND INFORMAL COMMUNICATIONS

DIFFUSION IN ORE GENESIS.

Sir: I beg to reply to the recent criticism of my paper on "Diffusion in Ore Genesis," made by Mr. Louis H. Smith in the December number of Economic Geology.

Mr. Smith suggested that "unwittingly" I had furnished laboratory evidence in support of Mr. Spurr's theory on the movement of matter, "miscalled 'a magma.'" My conception of the difference between Mr. Spurr's ideas and my own is that they are diametrically opposite. He conceives an ore-magma moving through a fissure to a seat of emplacement; but in my experiment I showed that mineral matter moved through water filling the pore spaces of rock. It had no carrier. Furthermore, it was not driven by any telluric force; and the radius through which I understand Mr. Spurr to admit diffusion is not of the same order of magnitude as that proposed in my paper. Also, it has long been known that diffusion proceeds readily through colloids; but the volume of colloidal matter in an ore-magma is in no way comparable with the volume of rock available to the type of diffusion demonstrated in my experiment.

In view of Mr. Smith's remarks I feel called upon to protest any effort to reconcile either my experimental results or my ideas on diffusion with the theory of ore-magmas. In fact, I think it important here to point out that diffusion is proposed as an antithetical interpretation of the phenomena of ore deposits. Inasmuch as Mr. Smith touches upon two vital matters in both theories, namely, metasomatism and vein inclusions, I will endeavor to point out more clearly the position of the diffusion conception. I will also briefly touch upon the zonal arrangement of ore deposits about a batholitic intrusion.

Metasomatism is a term originally created to mean replacement of one mineral substance by another, molecule-by-molecule; but in view of the default of any demonstration of such a phenomenon and the numberless conceded demonstrations that mineral replacements are typically grain-by-grain substitutions without volume changes, the meaning now generally understood to attach to the word is merely that of *replacement*. The original idea that the process was a chemical one seems generally to have given place to the tacit assumption that it is more physical than chemical in its nature. The reason for this is well illustrated by one of the innumerable examples, which is taken from the Cobalt district in Ontario, where slender smaltite veins may be found replacing conglomerate with sharp, plane, parallel walls, regardless of the various minerals contained in the various pebbles of the conglomerate traversed by the veins. Perhaps there is no objection to Mr. Smith's contention that the process if not molecular is at least atomic, if it is made clear what that means.

That metasomatism is the general rule in the formation of ore deposits is seen in the facts, (1) that cases where the walls of ore bodies have been thrust aside by the injection of the orebody are rarely if ever demonstrable, (2) that cases of consistent crustification are also rare, (3) that if ore and gangue or vein-matter are removed from their matrix by mining or imagination, the remaining open spaces by no stretch of the imagination could be conceived to have existed prior to the ore nor to have been created by displacement, and (4) that in the majority of ore deposits all stages of transition from country rock to ore can be found either in the main orebodies or in the weak associated mineralizations. In most cases the orebodies contain sheets or sheet-remnants of wall rock or else other fragmental inclusions of the wall rocks oriented parallel to the walls or to the wall structures or clearly transitional into wall rock by the gradual dwindling of mineral or gangue outward from the central region of the orebody.

In this connection I beg to call the attention of fellow geologists to the important utility of non-commercial mineralizations

which usually accompany the richer deposits. There are many illusions in natural phenomena, and more particularly in connection with mineralization; and where this process is most intense it has usually obliterated the successive stages of its origin; but these are clearly recognizable in the vicinity where mineralization has been impotent to disguise itself. In the associated non-commercial mineralizations therefore, one is to look for the key to the formation of the neighboring bonanzas. In such places ideas of injection and of crustification fade into mere fantasies. It is also important in studying the genesis of ores in a particular district to study all the weak non-commercial mineralizations which occur not only in the immediate vicinity of the paying orebodies but those of the region about, perhaps a mile or more away. What agencies delivered mineral and emplaced it in those numerous non-commercial occurrences? I propose that in such studies the hypothesis be entertained that the orebodies grew by marginal accretion, the mineral matter aggregating itself about centers or loci of metasomatism. Such a procedure would be a natural part of the mechanism of diffusion, for it is by precipitation that migration by diffusion is instituted and directed; but it has no place in the theory of ore-magmas.

An ascending ore-magma, whatever may be its content or condition, must have a limited capacity to permeate rock without displacement. No matter how great its hydrostatic head and temperature within the limits of reason, the laws of flow of fluids must control the rate at which it would move through the capillary and sub-capillary pore spaces of rock. In any such sluggish movement, especially where it is performing the work of replacement, its initial free energy content must soon be dissipated. This consideration is a serious drawback to the supposition that an ore-magma could produce a metasomatic vein of any considerable magnitude or extent. The energy content of a supposed magma could not persist during the extension of such a vein to the dimensions of known replacement veins.

We are next concerned with the matter of vein inclusions and the alternatives of their suspension in colloidal gel injected from

below, or their preservation as metasomatic remnants in a vein which by marginal accretion has grown around them. There are several difficulties in the way of the gel theory. Where there has been injection there has been expansion of wall formations about the injected bodies unless the walls yielded plastically. In any case the rigorous consequences of displacement must be discovered in the matching of walls, signs of compression in them, or signs of the expansion of their containing formations. Another consideration in connection with gels is the unreasonableness of the supposition that a mass or magma of gel could be transformed into a crystalline mass such as the usual vein-quartz. Transformations from opal to chalcedony are difficult enough to demonstrate, but from chalcedony or opal to crystalline quartz is more difficult no matter how large the time factor. Lastly there is the difficulty of identifying inclusions as truly foreign to the place where found in the sense of having ascended from below, or as being really oriented at variance with the walls or wall structures. In cases where the inclusions have ascended from below and are really rotated, it must be shown that their position and rotation are not due to pre-vein faulting movement. In cases where the inclusions are of local origin but are rotated, it is necessary to show that their rotation has not been due to the force of crystal growth during vein formation.

In many localities where dominant metasomatism would be conceded by all observers it would be easy to show that metasomatism frequently proceeds along reticulate surfaces or along lines of weakness parallel to vein walls and just within them, and that replacement thus inaugurated produces thin sheets or wedges of vein-matter which grow in extension of their edges and also laterally by marginal accretion. Avenues of growth thus established are extended and thickened in such a manner that in their reticulate pattern they coalesce and isolate fragments of wall rock. These fragments dwindle by replacement on all margins and gradually become small angular fragments imbedded in vein matter, or else, in the case of the lines of weakness parallel to the vein walls, the inclusions finally become thinned to sheets and

mere shadows of sheets of wall rock, giving the orebody a banded structure.

In regard to metalliferous zones, it is difficult to ignore the abundant evidence that exceedingly mobile pegmatitic and ultra-pegmatitic magmas emanate from segregated plutonic masses, and that these contain metalliferous sulphides. It is also difficult to ignore the equally abundant evidence that large quantities of metalliferous sulphides emanate in some manner from plutonic masses and are deposited in some manner in the neighborhood, often in a roughly zonal arrangement and often in massive veins; but there is a wide gap to span in attempting to project the magmatic state from pegmatite or even silexite to the genesis of mineral veins, however systematic the zonal arrangement.

Lawson[1] has shown it to be highly probable that meteoric waters in the neighborhood of a hot intrusion may have their circulation enormously stimulated by the igneous heat, and as a result acquire mineral matter from the mass and its aureole, thereby becoming potent in the formation of mineral deposits. In this connection strong supporting evidence is found in the geysers and hot springs whose total issue of water is vastly too great to be magmatic, although the heat and mineral content may be of magmatic origin.

The heat-aura of a plutonic intrusion may be conceived to surround it as an envelope deformed by variations in the conductivities of wall rocks to some extent, but more notably by channels of convection and emanation. Perhaps the zonal arrangement of metalliferous deposits about a plutonic mass represents the successive zones of mineral stabilities within such a deformed heat-aura, with the help of the heat-stimulated circulation of meteoric waters. Under such circumstances, circulation of mineral-bearing waters being conceded along trunk channels in fissure zones, perhaps diffusion would be adequate to convey mineral to seats of deposition and to facilitate the replacement processes.

It is significant as a matter of statistics that, of the world's ore

[1] "Ore Deposition in the Near Intrusive Rocks by Meteoric Waters," Univ. of Calif. Pub. Bull. Geol. Dept., Vol. 8, No. 9.

deposits, the cases which can by any approximately direct evidence be genetically related to magmatic segregation or anything in the general nature of an ore-magma are distinctly in the minority. Of the majority, those which are spatially and apparently genetically related to porphyries, which obviously are not differentiated, are easily preponderant. The statistical elaboration of this statement is obviously impossible in this place, and it is not pertinent to expand it too far in a broader sense at the expense of the point which I desire to make, which is that the relations of ore deposits in general are such as to have given Sandberger[2] good grounds for his nucleal conception of lateral secretion. Possible local sources of ore are abundant, provided only that a means of migration and concentration can be conceived; I have proposed diffusion for that role, and metasomatism as its crux.

ALFRED R. WHITMAN.

UNIVERSITY OF CALIFORNIA,
AT LOS ANGELES, CAL.

ON THE USE OF THE TERM DEUTERIC—A REPLY.

Sir: In a recent number of this journal, Mr. J. L. Gillson replied to a criticism of the use of the term deuteric in a paper[1] of which he was the senior author. I should like to take this opportunity to re-state the reasons for the criticism.

The difference in usage of the term reduces to a difference of interpretation of the article[2] by Sederholm, by whom the term was originally defined. The point which is especially in doubt is the interpretation of the phrase "belonging to the magma itself." Mr. Gillson applies deuteric to the changes produced by any part of a magma body on an already consolidated part of the magma. I discussed the use of the term with several persons who had read

[2] Untersuchungen über Erzgänge, 1882. Also S. F. Emmons, "Ore Deposits," p. 23, 1913, and others.

[1] Gillson, J. L., Callahan, W. H., and Millar, W. B., "Adirondack Studies: The Age of the Adirondack Gabbros, and the Origin of the Reaction Rims and Peculiar Border Phases Found in Them," *Jour. Geol.*, XXXVI., pp. 149–163, 1928.

[2] Sederholm, J. J., "On Synantetic Minerals and Related Phenomena," *Bull. de la Comm. Geol. de Finlande*, No. 48, 1916.

Dr. Sederholm's original paper, and it was agreed that, as defined, the term applied to the changes in the rock resulting from emanations derived by the crystallization of the rock itself, and therefore produced in the rock near the close of the period of crystallization. Such an interpretation is not unique: Holmes [3] says, "Deuteric, Sederholm, 1916.—A term applied to the alteration in igneous rocks produced during the later stages, and *as direct consequence of the consolidation of the magma of the rock.*[4] (Cf. Paulopost.)"

According to Mr. Gillson and co-authors, the changes in the rock to which they apply the term deuteric are due to "a distillation of volatile constituents," not released by crystallization of the magma of the rock, but coming from a magma at depth. However, the magma yielding the emanations occupies the same magma chamber as that from which the original rock was drawn. According to their idea of the formation of the alteration, and with the interpretation given above by Holmes and the writer, these changes would be secondary and therefore not deuteric.

Mr. Gillson draws some sanction for his use of the word deuteric from a paper by Colony.[5] However, Dr. Sederholm [6] himself protests against some of the extensions to the usage of the term deuteric proposed by Colony.

If the interpretation of the term deuteric as outlined by me is erroneous, I shall be pleased to be corrected. I think the misunderstanding brings out one point and that is the necessity for more concise definitions of such terms.

FRELEIGH F. OSBORNE.

UNIVERSITY OF IOWA,
IOWA CITY, IOWA.

[3] Holmes, Arthur, The Nomenclature of Petrology, p. 77, London, 1920.

[4] Italics mine.

[5] Colony, R. J., "The Final Consolidation Phenomena in the Crystallization of Igneous Rocks," *Jour. Geol.*, XXXI., pp. 169–178, 1923.

[6] Sederholm, J. J., "On Migmatites and Associated Pre-Cambrian Rocks of Southwestern Finland," *Bull. Comm. Geol. Finlande*, No. 77, Pt. 2, p. 88, 1926.

REVIEWS

The Coral Reef Problem. By WILLIAM MORRIS DAVIS. Pp. 596, figs. 227, bibliography, index. Amer. Geographical Society, Special Pub. No. 9. New York, 1928.

This is an exhaustive and authoritative monograph on the leading theories of coral reefs and the facts of the coral reef problem. It represents fifteen years of study by the author, and his field work has covered most of the coral reef regions of the globe. He advances much new evidence confirming the Darwin-Dana theory of the origin of atolls by subsidence. The book is written in the author's well-known clear style, though one detects special pleading in its pages. Beautiful photographs and many charts illustrate the pages, and of course there are many of the author's inimitable sketches. The book is finely printed and bound, and is a credit to the author and to the American Geographical Society.

ALAN BATEMAN.

Oil and Gas in Western Canada. By G. S. HUME. Pp. 152; Illust. 14. Geol. Surv. of Canada, Econ. Geol. Ser. 5, 1928. Price, 25 cts.

Following a brief and general review of the physiography and stratigraphical geology of the Great Plains, the publication consists of a series of reports on the individual oil and gas fields now known to exist in the region extending from Manitoba on the east, to British Columbia on the west, and north to Great Slave Lake and the MacKenzie River Basin in the North West Territories. The stratigraphy and structure are discussed in each case. The prospects of bringing several new fields into production are indicated by the application of the theory of Carbon Ratios as an index of the occurrence of oil and gas. This part of the publication was first published in the Bulletin of the Canadian Institute of Mining and Metallurgy, and, as may be recalled, caused considerable excitement in some sections at the time. The author makes a brief résumé of petroleum geology in its different aspects, as well as of the geophysical methods of prospecting for oil. The location of the wells, with brief remarks on each, is included in an appendix. Although the bulk of the report is of a descriptive nature, it makes interesting reading and is a source of information and reference.

LIONEL R. SIMARD.

The Geology of Arran. By G. W. TYRRELL. Pp. 292, illus., 42. Memoir, Geol. Surv. of Scotland, Edinburgh, 1928 (Dec.). Price, 6s 6d.

This island, a classic in British geology, recalls at once the names of noted workers who have helped to unravel its complexities, such as Hutton, Sedgwick, Murchison, Ramsay, Sorby, Teall, Geikie, Harker, Gregory, and Gunn. The present work brings together the previous investigations, particularly the unpublished work of Gunn. To it is added Dr. Tyrrell's own careful field and petrographic work. The old schists are described, and the old and new Red Sandstones are adequately treated. But the greatest interest centers in the igneous rocks, and especially the innumerable small intrusions that riddle the island. Their interpretation formed the storm center of some of the great geological controversies of the past, out of which evolved much of our modern petrology. The present work is a great contribution to the petrography of igneous rocks, and one that should be read by all students of igneous petrology.

ALAN BATEMAN.

Illinois Coal: A Non-Technical Account of Its Occurrence, Production and Preparation. By A. BEMENT. Pp. 112; figs. 50. Ill. Geol. Surv. Bull. No. 56. Urbana, Illinois, 1929.

This publication is a general information bulletin touching on various phases of the coal industry in Illinois. The geological chapter deals with the major features of stratigraphy and structure; it is brief, but contains a bibliographic footnote covering 22 State Survey titles of more specific import. The chapters on mining and preparation are up-to-date summaries of industrial progress.

Coal production and quality are treated by districts and counties, and include brief and simple explanatory matter as well as statistical data. Sixteen tables of statistics are amplified by seven maps and twelve graphs. Proximate analyses of coals from 223 mines in 41 counties, and ultimate analyses from 74 mines in 24 counties are given. Well chosen photographic and diagrammatic illustrations add to the informative value of the volume.

The style of this book is brief, simple, and eminently readable. The volume is not an important contribution to technical literature, which statement is made by way of praise and not of blame. A prefatory note states that the bulletin "has been prepared primarily for the public rather than the technical reader." For such a purpose, the book is good.

STERLING B. TALMAGE.

Structure of Typical American Oil Fields. A symposium on the relation of oil accumulation to structure. Vol. I., 1929. Pp. xvii + 510. Many maps and section. Amer. Assoc. Petr. Geol., Tulsa, Oklahoma. Price $5.00.

The subject matter of this volume is well defined in its title. It is a compilation of 30 papers on the structure of typical oil fields in Arkansas, California, Indiana, Kansas, Kentucky, Louisiana, Michigan, New Mexico, Ohio, Oklahoma, Tennessee, Texas and West Virginia. Each article describes in detail the dominant structure of the field with which it deals and illustrates the description with maps, sections and production graphs. The general geology of the district in which the field is situated is outlined and the relation of the productive portion of the field to the structure is discussed. In many of the articles decline curves for average wells are given, and from these the ultimate yield per acre is calculated.

Nearly all types of confining structures are illustrated and the relation of production to structure in each field is well shown.

There is very little that is new in the volume. Most of the facts recorded are well known to the students of the various fields. The book's great value is in the presentation in a clear and comprehensive manner of the geology of areas that illustrate different types of oil occurrences. Much of the new evidence cited in many of the articles indicates that the prevalent views as to the reason for the presence of oil in some fields are not correct. For some time they have been known to be incorrect by practical oil geologists, but contradictions of the older views have appeared in very few text-books. Faults are recognized as being responsible for the accumulation in many pools and unconformities in several. The belief that most oil is in anticlines or on terraces is badly shattered by the description of the various fields discussed in the volume, but the general principle of which this theory is an expression is substantiated. The pools are in the higher portions of the beds in which the oil occurs. Unconformities are described as being responsible for some of the pools, but in what way they served as reservoirs is not satisfactorily explained.

Most of the articles are thorough discussions of the areas with which they deal and give excellent mental pictures of their geology. In many of the fields faulting plays an important part in localizing the pools. In others sand lenses are the important reservoirs, and in others folds are the determining features.

The book is well printed and is abundantly illustrated with remarkably clear figures. It will be of great assistance to all students of oil geology whether in the universities or in the field.

W. S. Bayley.

BOOKS RECEIVED.

Outlines of Geology Southeast of Lake Victoria: Short Paper No. 1, by F. B. WADE, 24 pp., map. Lupa Gold Field; Short Paper No. 2, by D. R. GRANTHAM, 6 pp., 2 maps. Kigugwe Copper Deposit, Short Paper No. 3, by G. M. STOCKLEY, 8 pp., map. Published by Geological Survey, Tanganyika Territory, Dodoma, Africa, 1928.

A new series of short papers making available the geology and mineral resources of areas of interest. Concise; commendable.

Geological Survey of Tanganyika, Annual Report, 1927, by the Director, E. O. TEALE. 60 pp., 2 maps. 1928 (Feb., 1929).

Administrative; geological reports by staff; includes map of geology known to date.

Bituminous Sands of Northern Alberta, Experimental Drilling and Paving Operations, 1927. By S. C. ELLS. Pp. 60, illus. 18. Canada Mines Branch, Mineral Resources and Mining Industry, No. 694, Ottawa, 1928 (Mar., 1929).

Gives methods of drilling and use for paving.

List of Publications on the Geology of Illinois, with index. Illinois Geol. Survey, January, 1929.

Limestone Resources of the Pontiac-Fairbury Region, Illinois. By J. E. LAMAR. 27 pp. Ill. State Geol. Survey, Rept. of Inves. No. 17, 1929 (Mar.).

General geology and economic uses of the limestone.

Illinois Petroleum—The Dupo Oil Field. By A. H. BELL. (14 pp.) Petroleum Production and Development in Illinois during 1928, by G. F. MOULTON (4 pp.). Ill. State Geol. Survey, Press Bull. 17, 1929 (Mar.).

Surface Water Supply of the United States: Part IX, Colorado River Basin. 159 pp. U. S. Geol. Surv. Water Supply Paper 589, 1928 (Feb., 1929).

SCIENTIFIC NOTES AND NEWS

Arthur Bevan, assistant professor of geology at the University of Illinois, has been appointed State Geologist of Virginia to succeed W. A. Nelson. He will enter on his new duties in June.

Ira B. Joralemon, of San Francisco, has gone to Europe on a business trip.

Alan Bateman, of Yale University, will leave May 1 for South Africa via London and East Africa, to visit the copper deposits of Katanga and Northern Rhodesia before attending the meetings of the International Geologic Congress during July and August.

Frank L. Hess, chief engineer of the Division of Rare Metals and Non-Metals of the U. S. Bureau of Mines, sailed on the *President Cleveland* from San Francisco on March 15 for a trip of about nine months, to include Shanghai, Canton, the Malay Peninsula, Burma, India, and probably Russia and other European countries.

Cyril W. Knight is making an examination of the Dunkin Gold Mines properties, Narrow Lake section, Patricia district, northern Ontario.

J. A. MacDonell, of Lima, Ohio, expects to attend the International Geologic Congress in South Africa this summer.

Charles H. White, of San Francisco, Cal., has gone to South Africa on professional business.

J. J. O'Neill has been made Dawson Professor of Geology and head of the Department of Geology at McGill University, Montreal, Canada.

F. G. Pardee and W. Osgood, appraisal geologists for the State of Michigan, have been appraising the mining properties in the Michigan copper district.

A. M. Gaudin, of the University of Utah, will become connected with the Montana School of Mines on July 1, as research professor of ore dressing.

W. Spencer Hutchinson has returned from a trip to Peru and Chile.

Carl H. Beal, A. H. Heller, and Grant Corby have opened an office in the Quinby Building, Los Angeles, Cal., as petroleum engineers and geologists.

Marden W. Hayward is consulting engineer for Compania Minera de Penoles, S. A., and is also continuing his work in their geological department.

Olaf P. Jenkins is conducting geological research work in California in connection with Stanford University.

Colin C. Rae, of the U. S. Geological Survey, has resigned and taken up work for the Skelly Oil Co., Tulsa, Okla., in the geological department.

A second air mapping expedition will go to southeastern Alaska this summer. The work will be undertaken by the Navy Department, but R. E. Sargent of the U. S. Geological Survey will be associated with it in an advisory capacity.

Stanley R. Moore, of Wallace, Idaho, has returned from a trip to Alaska after examining mines in the Chichagof and adjoining districts.

The U. S. Department of the Interior announces that potash has been struck by three more core tests in Texas. All three of the holes penetrated numerous beds of polyhalite interbedded with halite and some anhydrite. Probably none of the beds are of commercial value, though some are thick enough if they were richer, and others are rich but too thin. The tests were in Crockett, Reagan, and Glasscock counties.

The Annotated Bibliography of Economic Geology is now being assembled for the press.

The XVth International Geological Congress, to be held in South Africa, announces a new excursion, C–22, to Northern Rhodesia and Katanga, starting from Victoria Falls August 19 and returning there August 28.

A unique monument on the Pennsylvania State College campus, known as the Polylith, consists of 281 samples of stone procured from about 150 localities in the State. These are chronologically arranged, forming a column six feet square at the base and 33 feet in height, and calculated to weigh approximately fifty-three and one half tons. Since this affords a criterion for estimating weathering qualities, it attracts building specialists and geologists from all parts of the country.

The West Virginia Academy of Science held a meeting at Charleston April 26 and 27.